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ABSTRACT

This unit is one of a group of units written to fit the Certificate of Sixth Year Studies (CSYS) chemistry course, but it could also be used in most Sixth Form courses. It includes: (1) a reading for students to complete at home before starting the main package; (2) a collection of group and/or individual student activities; (3) background notes for teachers and two background papers ("The Story of Titanium" and "Titanium and Its Alloys"); and (4) answer sheets which are attached to part three. These materials are intended to cover the thermodynamics and metals chemistry sections of the CSYS syllabus. (DH)

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TITANIUM

This unit is one of a group of units written to fit the Certificate of Sixth Year Studies course but could certainly find a place in most Sixth Form courses.

The series has been written by a group of teachers, college lecturers, university lecturers and industrialists.

It has been supported financially by the Education Appeal Fund of the Royal Society of Chemistry and the Education for the Industrial Society Group of the Scottish Curriculum Development Service and has received the approval of the Chemistry Panel of the Scottish Examination Board.

It is hoped that this will be used in an interactive way to give pupils the experience of making decisions for themselves on the basis of their chemical knowledge and the knowledge of other disciplines, so that they may truly see that the decisions of chemical industry are of necessity - multi disciplinary.

We realise that this unit will not be perfect and we would welcome helpful criticism so that later editions can be improved.

Dr. A.H. Johnstone
General Editor.

The writers of this unit were:-

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CSYS PACKAGE ON TITANIUM

CONTENTS OF COMPLETE PACKAGE

Part 1 - in B L U E is for your pupils to read at home before starting the main package.

Part 2 - in P I N K is the main part. It involves group work on several occasions.

a. small CSYS classes should work as individuals
b. larger classes could work as individuals, or in pairs.

Part 3 - in Y E L L O W contains background notes for teacher presentation. You should EITHER make ohp transparencies of the last 2 sheets, or duplicate sufficient copies to which your pupils can refer during your presentation.
In addition, there are 2 background papers for your interest and information.

Part 4 - in W H I T E provides sheets with the answers to most of the numerical work. You should tell your pupils to compare their answers once they have completed each table.
Elsewhere in the package, the answer is given on the page following: it may be necessary for you to tell your pupils not to turn over until they have written their answer down.

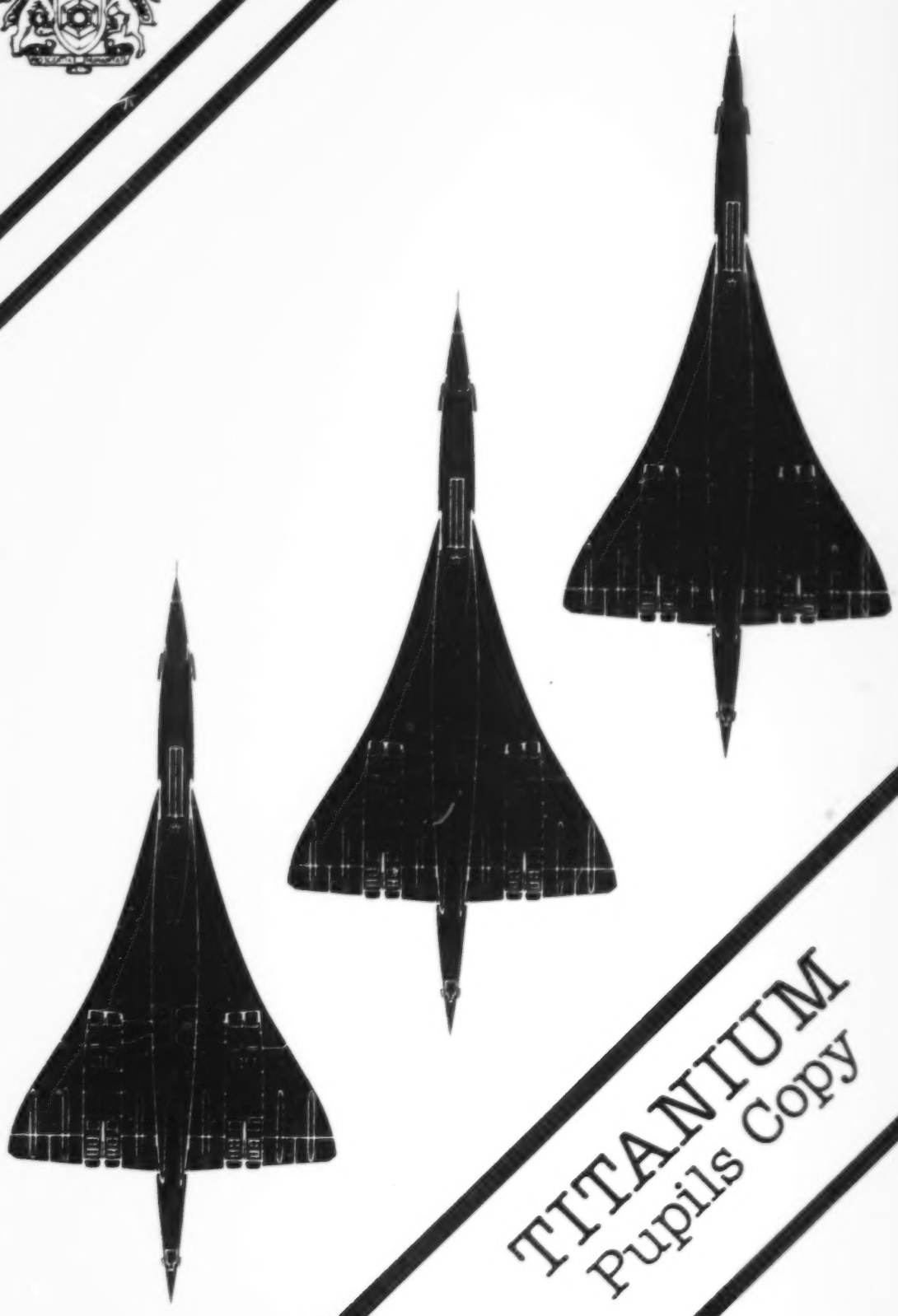
If you wish to retain the packages for use in future years, tell your pupils not to write the answers on them, but on separate sheets of paper.
Part 2, sheet 9 , could be duplicated and left with the pupils as a permanent record for their notes.

The package is intended to cover the following sections of the CSYS syllabus -

Thermodynamics section 3.9 (Ellingham Diagram).
Metals Chemistry - section 7.2(c) (part)
(In the trials, the majority of schools felt that it taught Ellingham Diagrams satisfactorily, but a minority felt that this should be taught first, and the package used as consolidation and revision).

TIME: For Parts 2 - 4, 2 double periods (maximum)

Time could be saved by giving out the calculations on Pink Sheet 1 to be done as homework. Do not, however, give out the whole pink booklet to class members to take home.



TITANIUM
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TITANIUM - THE AEROSPACE METAL

PART 1: INTRODUCTION

Probably no other metal can match the meteoric rise of titanium from being a laboratory curiosity about 30 years ago to its present position in the forefront of technology. The metal has earned its position because of its unique combination of desirable properties:

high strength to weight ratio

high strength at high temperature

low thermal expansion

outstanding resistance to corrosion.

Study the accompanying tables which show some important properties of titanium and a titanium alloy in comparison with iron and aluminium and 2 of their typical alloys.

Selected Properties of some Metals and their Alloys.

Metal	MP(^{o}C)	Density (g cm^{-3})	Standard Reduction Potential (V) *
Aluminium	660	2.7	-1.67
Iron	1335	7.86	-0.04
Titanium	1660	4.51	-1.75

* for the reaction $M^{3+}_{(aq)} + 3e \longrightarrow M_{(s)}$

Relative Strengths of Typical Alloys.

Alloy \ Temperature ^{o}C	100	300	500
Aluminium Alloy	0.56	0.09	-
Steel	0.57	0.49	0.39
Titanium Alloy	0.85	0.72	0.67

Note: Titanium is the fourth most widely used structural metal, coming after iron, aluminium and magnesium.

From these tables, you will see that

* titanium has a relatively high melting point
* titanium has a lower density than steel
* titanium is about 50% stronger for a given weight than steel
* titanium retains its strength at high temperature better than steel, and much better than aluminium
* titanium is a reactive metal,

As a result, titanium alloys are employed in situations where its high strength - low density, and retention of strength at high temperature, gives it a decided advantage over other metals. In the early 1960's, 95% of titanium production was devoted to aircraft manufacture, most of this being used in the turbines of jet engines for military aircraft.

The possibility of improved performance resulting from the use of titanium components has led to a number of governments investing in this strategic metal. As production and fabrication techniques have improved over the years, civil aircraft have increased their share of production. A typical example is the turbine of the RB211 engine used to power the Lockheed Tri-Star. Titanium alloys are used extensively for such components as compressor blades, discs, casings, by-pass ducts, cowlings and exhaust shrouds. Air frame uses of titanium alloys include fasteners, hot air ducting,and heat shields.

The Russians have developed another military use for titanium - a submarine with a titanium hull. Because of the high strength and low density of the metal, the submarine is able to dive much deeper than a similar conventional submarine.

Titanium is a reactive metal. Oxygen is usually the first element with which it comes into contact, but they combine almost instantaneously, forming a tough and unreactive film of titanium oxide. This layer gives titanium its corrosion resistant properties in the same way that aluminium oxide protects aluminium. It should be noted, however, that appreciable quantities of oxygen present in the bulk of the metal make it too brittle to be useful. The normal permitted levels are 0.18 - 0.25 % by volume. Thus one of the major problems in titanium manufacture is ensuring that little oxygen, and indeed little other non-metals,and iron, come into contact with it during production.

As would be expected, titanium is more resistant to corrosion in oxidising than in non-oxidising media. Excellent resistance is exhibited over a wide range of temperatures and concentrations against metal chlorides, acids and alkalis in solution. It is thus used in the chemical industry as a lining or as a primary constructional material for vats, driers and reactor vessels, and for pumps, valves and for many other components.

Titanium's superb resistance to corrosion in seawater has led to the largest use for the metal outside the aerospace industry. It is used to construct heat exchangers for power stations and desalination plants. Tubes in power station heat exchangers made from steel corrode rapidly in this environment and evertually fail: this tubing is now being made from titanium.

Titanium also plays its part in the development of the North Sea, where heat exchangers with titanium tubes using sea water as a coolant are installed on a "fit and forget" basis, i.e. equipment made from titanium is installed in crucial areas where unscheduled shutdown for repair would be very expensive indeed. However, recent experience by offshore operators has shown that

* titanium alloys in contact with other metals such as steel can give rise to serious corrosion, because the more reactive steel corrodes sacrificially to protect the titanium

* titanium and its alloys foul seriously in sea water at low flow rates (less than 1 m sec^{-1}). This is in contrast to copper based alloys, where copper ions produced in sea water reduce the rate of local fouling by barnacles, seaweed etc. by poisoning them.

Another field in which the passivity of the titanium oxide layer is beginning to be utilised is in medicine, where titanium is used for surgical and dental implants.

It is interesting to note that non-aerospace uses now account for about half of titanium production. This proportion will continue to increase.

One hundred years ago, aluminium was an expensive and rarely used metal, but now it plays a major role in industry and in our day-to-day lives. Twenty years ago, titanium was similarly rare and expensive. Its use is now becoming widespread, and it undoubtedly has considerable further potential.

Occurrence.

Titanium is the ninth most abundant element in the Earth's crust, occupying 0.6%. It is almost always associated with oxygen in the natural state. Economically viable deposits are found in Norway, Sweden, Finland, South Africa, U.S.S.R., North and South America, and Australia. The three main ores of titanium used are rutile, ilmenite and titanomagnetite.

Rutile is the purest form of titanium oxide, containing 91 to 99% of the oxide, along with small amounts of aluminium, calcium, chromium, iron, magnesium, silicon, sodium and vanadium. Australia accounts for 90% of the rutile produced in the Western World. The other two ores are more abundant and therefore cheaper, but they have a high iron content which gives rise to problems in the extraction of titanium.

Not all the rutile and ilmenite mined is used to produce metal; more than 60% of all the world's rutile and 80% of the ilmenite is used as a source of titanium oxide pigment to improve the opacity and colour of paint, plastics and paper.

Extraction.

The main theme of this topic is the extraction of titanium from its ores. However, let us first remind ourselves of how other metals are extracted. The metals of ancient times, such as copper, lead and zinc were relatively easy to obtain from their ores. For example, in the blast furnace, coke produces carbon monoxide and this reduces the iron oxide:

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

The extraction of more reactive metals such as aluminium, magnesium and sodium had to await the discovery of electrolysis in the nineteenth century. For example, magnesium is obtained by electrolysis of its molten chloride $MgCl_2$:

At the negative electrode, $Mg^{2+} + 2e \longrightarrow Mg$

At the positive electrode, $2Cl^- \longrightarrow Cl_2 + 2e$

An alternative process is displacement by a more reactive metal. For example, chromium is obtained from its oxide by heating with aluminium powder

$$Cr^{3+} + Al \longrightarrow Cr + Al^{3+}$$

Three possible methods of reduction to titanium metal should be considered:

* reduction by a non-metal, e.g. carbon or hydrogen
* electrolysis of a molten compound
* displacement by a more reactive metal, and its regeneration.

Consider these three methods, bearing in mind:

* Is direct reduction theoretically possible?
* The importance of obtaining PURE titanium, as its properties are adversely affected by impurities and especially by non-metals such as oxygen and carbon.
* Electrolysis requires a compound which can form an electrolyte.
* The economics of the process are important, and the possibility of recycling byproducts has to be considered.

From your present knowledge, write down - on a separate sheet of paper - the method or methods you think most likely to be used for titanium. Give brief reasons for your choice.

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Temperature and Reaction

The next part of this package involves calculating the temperature at which a reaction <u>becomes</u> feasible, i.e. when $\Delta G^\circ = 0$ (see footnote).

The following is included as revision, and should already have been covered in class.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

When $\Delta G^\circ = 0$, $T\Delta S^\circ = \Delta H^\circ$

i.e. $T = \dfrac{\Delta H^\circ}{\Delta S^\circ}$

Let us use this to find out if hydrogen can reduce aluminium oxide to the metal.

From data books we get

	$Al_2O_{3(s)}$	$H_{2(g)}$	$Al_{(s)}$	$H_2O_{(g)}$
ΔH°_f ($kJmol^{-1}$)	-1669	0	0	-242
S° ($JK^{-1}mol^{-1}$)	51	131	28.3	189

We put these values in a balanced equation:

$$Al_2O_{3(s)} + 3H_{2(g)} \longrightarrow 2\,Al_{(s)} + 3H_2O_{(g)}$$

ΔH°_f -1669 0 0 -726 change = 943 $kJmol^{-1}$ i.e. 943 x 1000 $Jmol^{-1}$

S° 51 393 56.6 567 change = 179.6 $JK^{-1}mol^{-1}$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{943 \times 1000}{179.6}\ K$$

$$= 5251\ K \text{ (or } 4978^\circ C)$$

This means the reaction becomes feasible at this (high) temperature.

It is high because of the relatively high and unfavourable ΔH° term.

In practice, it is so high that hydrogen cannot be used to reduce aluminium oxide - as you should have known in the first place! In any case, all the substances in the equation are gases at this temperature, so the calculated temperature is meaningless.

<u>Footnote:</u>

Remember that ΔG° is related to the equilibrium constant K by $\Delta G^\circ = -RT\log_e K$ and thus $K=1$ when $\Delta G^\circ = 0$, the situation considered above.

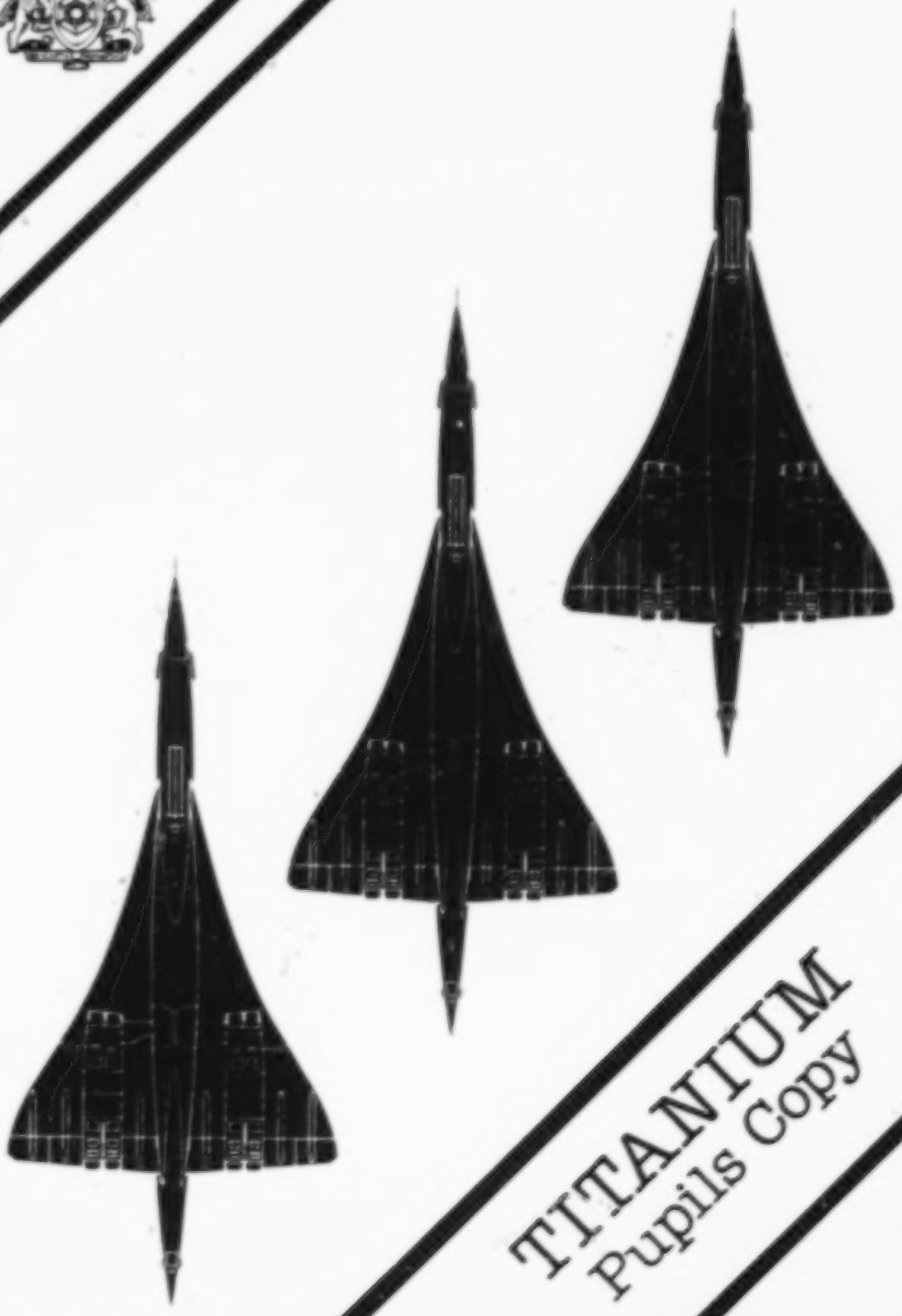
In terms of concentration $K = \dfrac{[\text{products}]}{[\text{reactants}]}$ and thus a negative ΔG° for a reaction means that [products] > [reactants], i.e. equilibrium favours products.

The more negative is ΔG°, the further the equilibrium is in favour of products.

The temperature calculated above is therefore the temperature <u>above which</u>

[products] > [reactants]

This situation would clearly be desirable for an economic industrial process.



TITANIUM
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PART 2A: POSSIBLE METHODS OF REDUCTION OF TiO_2

You have just read that titanium has advantages in use over both aluminium and steel. Its big disadvantage is its high cost compared with other metals.

Let us consider how titanium can be obtained from purified TiO_2. Let us, for the moment, exclude electrolysis.

Carbon, which works so well for iron, is an obvious choice as reductant, but the greater reactivity of titanium may mean having to use something more reactive, such as magnesium. We shall also consider hydrogen, which normally reduces the same metal oxides as carbon.

Consider, then, the following substances, to find out which are capable of reducing TiO_2 to the metal:

(i) C giving CO_2 i.e. $C + O_2 \longrightarrow CO_2$

(ii) C giving CO i.e. $2C + O_2 \longrightarrow 2CO$

(iii) CO giving CO_2 i.e. $2CO + O_2 \longrightarrow 2CO_2$

(iv) H_2 i.e. $2H_2 + O_2 \longrightarrow 2H_2O$

(v) $Mg_{(s)}$ i.e. $2Mg_{(s)} + O_2 \longrightarrow 2MgO$

or perhaps (vi) $Mg_{(g)}$ i.e. $2Mg_{(g)} + O_2 \longrightarrow 2MgO$

1. Your teacher will allocate these jobs round the class. Each of you is expected to calculate at least two.

2. For those that you are doing,

   a Write a balanced equation for the reduction.

   b Write in appropriate figures from the Appendix at the end of the booklet for

   $$\Delta H_f^\circ \text{ and for } S^\circ$$

   c Calculate the temperature at which the reaction becomes thermodynamically feasible, using the relationship

   $$T = \frac{\Delta H^\circ}{\Delta S^\circ} \text{ K}$$ (Remember to use the same units for ΔH° and ΔS°)

   d Check that the substances in the equation are in their correct physical state (solid or liquid or gas) at the calculated temperature.

   e Decide whether the particular reaction is feasible above or below the calculated temperature.

3. When all the calculations are finished, discuss your results with the others, and complete the following table, on a separate sheet of paper or on the blackboard if your teacher wishes.

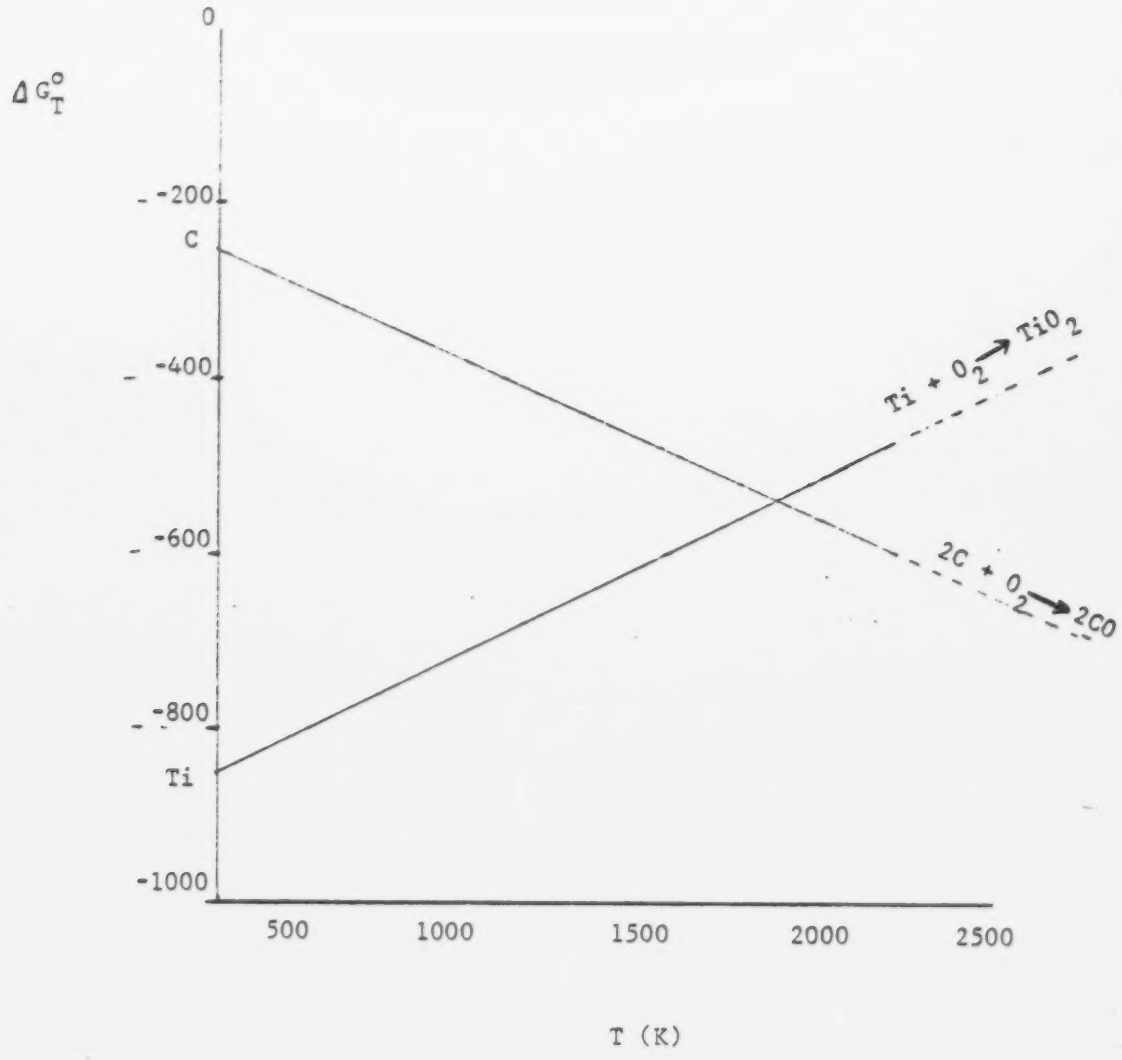
TABLE 1.

Reaction	Feasible T (K)	Is it feasible above or below this T?
$TiO_2 + C \longrightarrow Ti + CO_2$		
$TiO_2 + 2C \longrightarrow Ti + 2CO$		
$TiO_2 + 2CO \longrightarrow Ti + 2CO_2$		
$TiO_2 + 2H_2 \longrightarrow Ti + 2H_2O$		
$TiO_2 + 2Mg_{(s)} \longrightarrow Ti + 2MgO$		
$TiO_2 + 2Mg_{(g)} \longrightarrow Ti + 2MgO$		

4. One important factor in choosing which of the reductants will be most economical is temperature. Bearing this in mind, tick the one in the table you think most likely to be used.

When you have done this, go with your completed table to your teacher, who has a copy of the table with the answers filled in.

Graph 1: Ellingham Diagram for CO and TiO_2



Note:
Units are kJ per mole of O_2, so that

equations can be added or substracted.

Ellingham Diagrams

The method you have just used is tedious and time consuming, particularly if the physical state of one or more of the substances concerned is not known initially.

Your calculations above seek to find the temperature at which the overall ΔG° for the reaction changes from positive to negative, i.e. is zero.

Ellingham diagrams plot ΔG°_{T} (i.e. ΔG° at a temperature T) against T, and enable the feasibility temperature to be read off directly. Look at the first Ellingham diagram, Graph 1, which gives ΔG° values for the two equations:

$$2C + O_2 \longrightarrow 2CO$$

and

$$Ti + O_2 \longrightarrow TiO_2$$

Since we wish to make titanium, we shall require to reverse the second equation, and reverse the sign for the values read from the diagram for this reaction. Examine Graph 1, and read off information from it to fill in the gaps in Table 2, or on a separate sheet if your teacher wishes. Readings for the graph can be to nearest 10kJ. Work in the same groups as before.

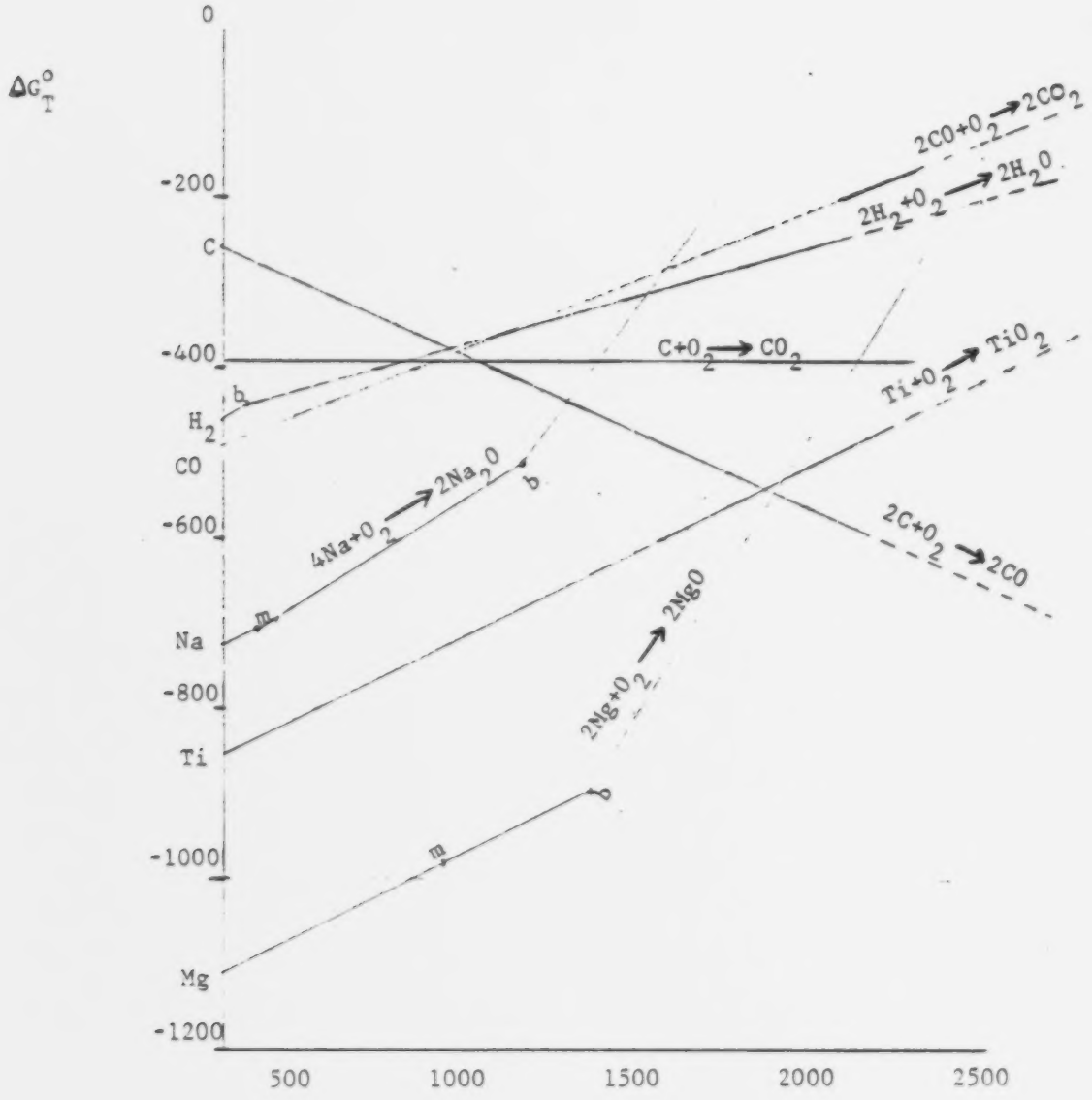
TABLE 2

	ΔG°_{500}	ΔG°_{1000}	ΔG°_{1500}	ΔG°_{2000}
$2C + O_2 \longrightarrow 2CO$	-290			
$TiO_2 \longrightarrow Ti + O_2$	+810			
Adding these gives: $TiO_2 + 2C \longrightarrow Ti + 2CO$	+520			
Feasibility	No			

All figures in $kJmol^{-1}$

When you have completed this, refer once again to your teacher, who has a copy of the completed table.

Graph 2: Ellingham Diagram for Selected Oxides



Units : kJ per mole of O_2

m = melts

b = boils

Thus the reaction becomes feasible between 1500K and 2000K.

By inspection of Graph 1, write down the approximate temperature at which the reaction does become feasible. You will find the answer at the foot of the next page.

Look back to find the temperatures that you calculated.

There is reasonable agreement : discrepancies may arise from difficulties in calculating S° values, with different sources giving different values.

You will see that

below 1870K, TiO_2 is favoured

above 1870K, Ti is favoured

i.e. lower line goes as written, driving upper line in reverse.

(You will find later - in Graphs 3 and 4 -that the two lines concerned do not always intersect; the same rule, however, still applies).

Using the information on the second Ellingham diagram, Graph 2, write down the approximate feasibility temperatures using the following reactions for the reduction of TiO_2.

TABLE 3

	Feasibility temperature from diagram	Is it feasible above or below this temperature ?
$2C + O_2 \longrightarrow 2CO$		
$2Mg + O_2 \longrightarrow 2MgO$		
$C + O_2 \longrightarrow CO_2$		
$2CO + O_2 \longrightarrow 2CO_2$		
$4Na + O_2 \longrightarrow 2Na_2O$		
$2H_2 + O_2 \longrightarrow 2H_2O$		

When you have completed this, refer again to your teacher to check your answers.

Conclusion

We have shown that the following methods of reducing TiO_2 merit further consideration:

* reduction with carbon
* reduction with magnesium, or another reactive metal
* with always the possibility of electrolysis.

PART 2B THE INDUSTRIAL PROCESS

The major problem in the reduction process is the high reactivity of titanium, and its readiness to form compounds with oxygen, nitrogen, carbon, silicon, iron and hydrogen. Unlike most other metals, titanium forms an extensive solid solution with oxygen. While small amounts of oxygen add useful strength to titanium, larger amounts lead to unacceptable embrittlement, along with a loss of corrosion resistance and ductility. The absorption of such non-metals (except hydrogen) is irreversible, and so in any extraction process, contact of the hot metal with the gases in air must be prevented.

As a result, NO method of producing titanium directly from its oxide is suitable, as removal of the absorbed oxygen is not possible. The oxide must first be converted to a titanium compound involving none of the 'problem' elements, and which can be easily purified. Because of the strong affinity of the metal for oxygen, the element to displace the oxygen must be reactive.

From your knowledge of the trends in reactivity in the periodic table, write down the names of some non-metallic elements that could displace the oxygen from TiO_2.

....

Which of these is most likely to be successful?

.....

Are there any very serious problems in handling this element?

.....

If your answer is "No" write the name of the element in the space below.
If your answer is "Yes", write down another element from your original list which you now think could be suitable.

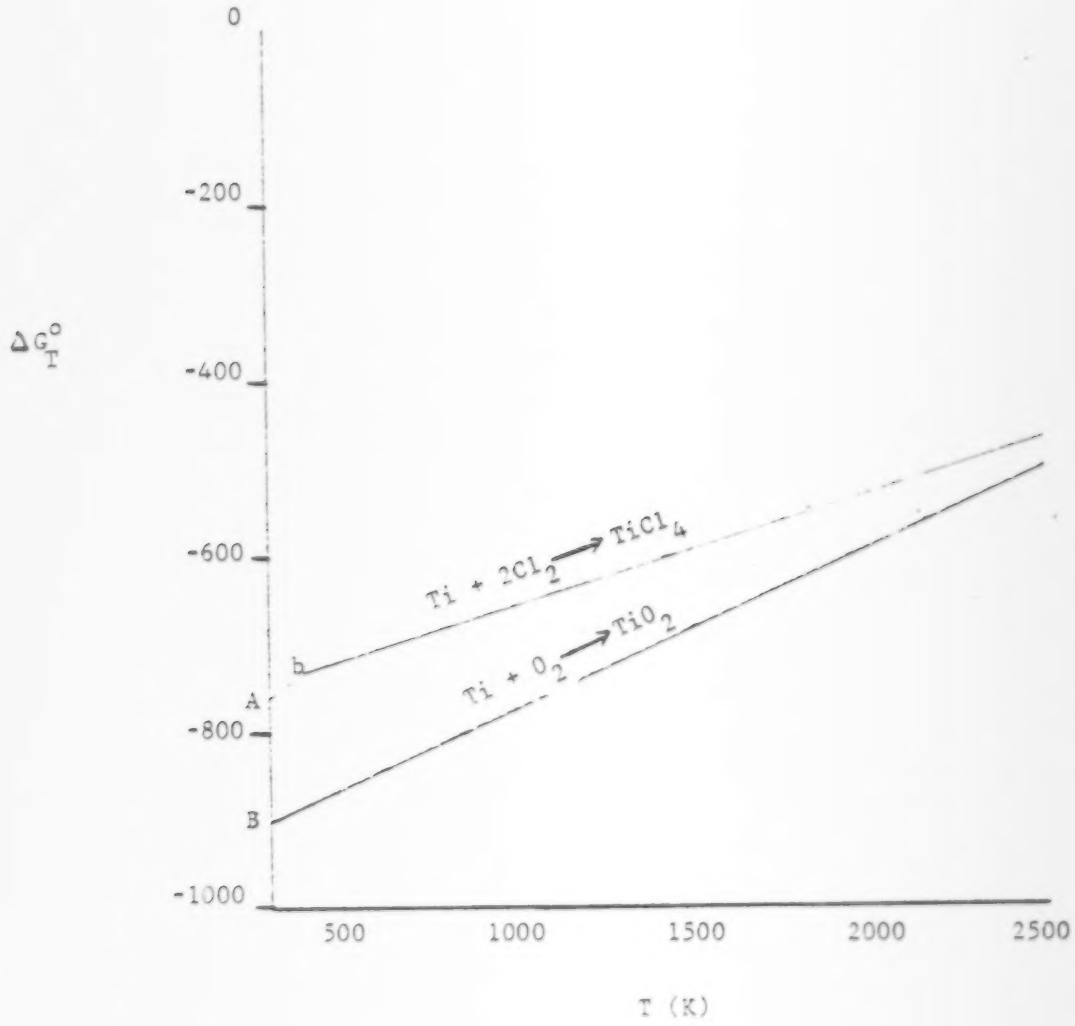
.....

From previous page:-

Answer approx. 1870 K

This is where the two lines concerned intersect.

Graph 3: Ellingham Diagram for TiO_2 and $TiCl_4$



Units : kJ per mole of Ti

You should have finally selected chlorine. Fluorine is the element which has to be excluded because of the dangers of handling, and because it is in fact too reactive.

Examine the Ellingham Diagram for TiO_2 and $TiCl_4$, Graph 3.

Line A represents the formation of one mole of $TiCl_4$ i.e.

$$Ti + 2Cl_2 \longrightarrow TiCl_4$$

and

Line B represents the formation of one mole of TiO_2, i.e.

$$Ti + O_2 \longrightarrow TiO_2$$

If these reactions are combined (by reversing reaction B), the resulting equation represents the chlorination of one mole of TiO_2:

$$TiO_2 + 2Cl_2 \longrightarrow TiCl_4 + O_2$$

These lines do not meet within the temperature range shown, and the reaction is not feasible within the given temperature range. Calculation by the method used earlier shows that it is not feasible at any temperature, as both enthalpy and energy terms favour TiO_2 (See footnote A).
Extra energy is required, and this is achieved by the addition of carbon.
This combines with the oxygen in the last equation

$$TiO_2 + 2Cl_2 + 2C \longrightarrow TiCl_4 + 2CO$$

Ellingham diagrams are not convenient for such reactions involving 3 reactants and the calculation method is preferable. The figures are set out as footnote B: these show that both the enthalpy and entropy changes are favourable, and so the reaction is feasible at all temperatures.

In practice, some carbon dioxide is also produced, and some chlorination of the oxides of carbon also takes place to produce phosgene ($COCl_2$). The process is carried out in an atmosphere of argon, at 700°C to 1000°C.

The necessity for high purity titanium has already been stressed. This means -

a) using a high grade ore - in practice rutile (91-99% TiO_2) - and separating it from other rocks present

b) purifying the $TiCl_4$ made from this TiO_2 before reduction to the metal. $TiCl_4$ boils at 409K, and can be readily purified by distillation.

Footnote

A.

	TiO_2	+ $2Cl_2$	⟶	$TiCl_4$	+ O_2	
ΔH_f°	-912	0		-750	0	change = +162 kJmol^{-1}
S°	50.2	446		253	205	change = -38.2 JK^{-1}mol^{-1}

B.

	TiO_2	+ $2Cl_2$	+ $2C$	⟶	$TiCl_4$	+ $2CO$	
ΔH_f°	-912	0	0		-750	-222	change = - 60 kJ mol^{-1}
S°	50.2	446	11.4		253	396	change = +141.4 JK^{-1}mol^{-1}

20 20

Purification of $TiCl_4$

Impurities in rutile include the oxides of aluminium, calcium, chromium, iron, magnesium, silicon, sodium and vanadium. Chlorination converts these to their chlorides, which will be present along with the $TiCl_4$. These have to be separated by distillation.

Boiling Points of Chlorides (K)

HCl 188													
LiCl 1655	$BeCl_2$ 765											BCl_3 285	$COCl_2$ 281
NaCl 1686	$MgCl_2$ 1685											$AlCl_3$ 451s	$SiCl_4$ 331
KCl 1773 s	$CaCl_2$ 2273	$ScCl_3$ 1100 s	$TiCl_4$ 409	$VOCl_3$ 400	$CrCl_3$ 1300	$MnCl_2$ 1190	$FeCl_3$ 592 d	$CoCl_2$ 1050	$NiCl_2$ 1246 s	$CuCl_2$ 1263 d	$ZnCl_2$ 1005	$GaCl_3$ 473	$GeCl_4$ 357

Notes:

1. The simple chlorides of vanadium are unstable, and $VOCl_3$ is the compound formed by chlorination.

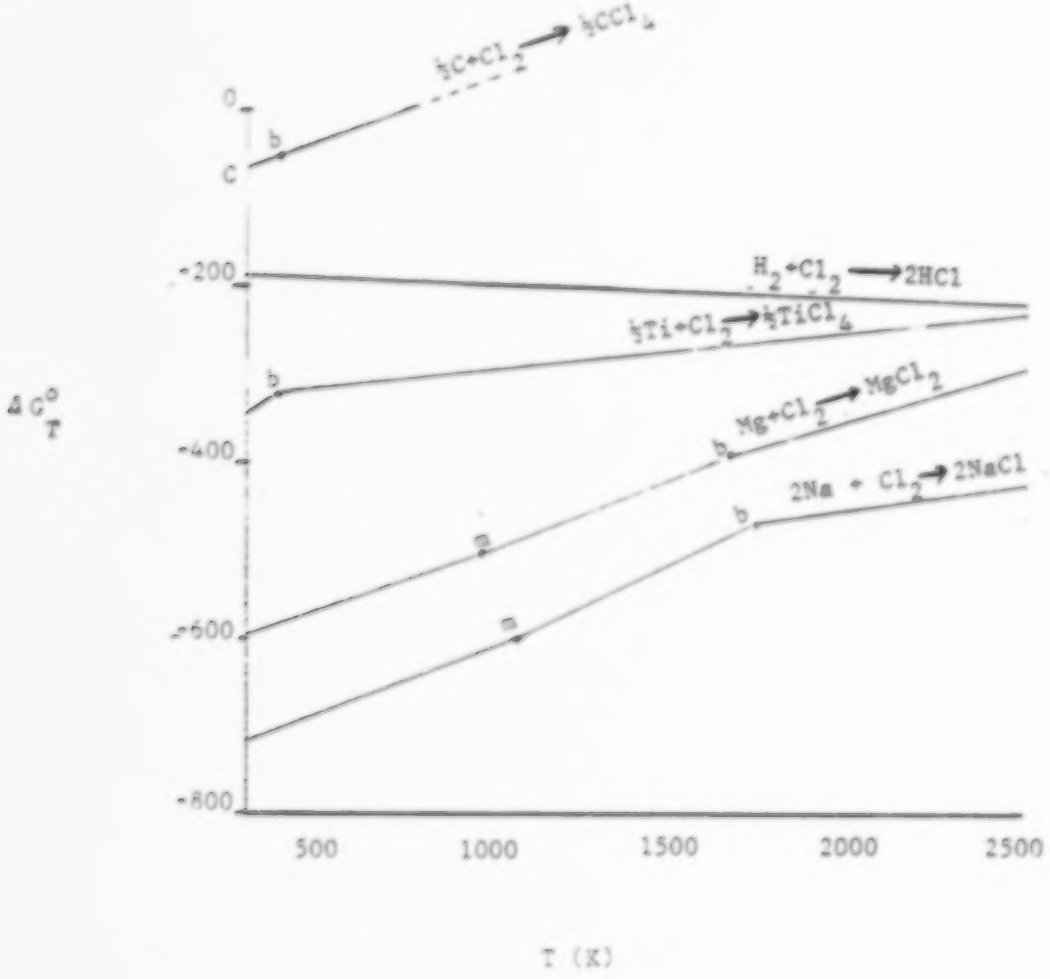
2. s : sublimes
   d : decomposes

Which two of these chlorides will be the most difficult to separate from the $TiCl_4$ by distillation?

(a) ..... (b) .....

(You will find the answer at the top of page 8)

Graph 4: Ellingham Diagram for Selected Chlorides



Units : kJ per mole of Cl_2

Answer: $VOCl_3$ and $AlCl_3$

The chloride which causes the greatest problem is vanadium oxychloride ($VOCl_3$). It is removed by reduction to the less volatile $VOCl_2$ using copper, or precipitated as a sulphide using hydrogen sulphide. Aluminium chloride can be removed by the addition of a trace of water, and separated as its hydroxide by filtration.

Note: Ilmenite is a far cheaper and more abundant titanium ore, but it is not used for this process because it contains large amounts of iron oxides. These not only use up large quantities of chlorine, but the $FeCl_3$ produced would rapidly choke the outlet of the chlorinator and stop the plant working. This is why the more expensive rutile is used.

Reduction of Titanium (1V)Chloride

Study the Ellingham diagram for selected chlorides, Graph 4.
What elements would reduce $TiCl_4$ readily, i.e. at reasonable temperature?

.....

If you were to consider using a temperature greater than 2500K, what other element is possible?

.....

Suggest some factors which might influence the choice of element

.....

.....

Another possible method of reducing $TiCl_4$ is by electrolysis. Its low melting point would be an advantage in reducing costs as it would not have to be heated in order to melt it. However, its low melting point indicates that the bonding is covalent rather than ionic. There are no ions present - it is a non-conductor and thus electrolysis of $TiCl_4$ cannot work.* Attempts have been made to reduce Ti(1V) to a lower oxidation state, in which the bonding would be ionic, and then to carry out electrolysis. So far, none of these attempts has produced an economical process, i.e. electrolysis of titanium compounds is NOT used.

As far as displacement is concerned, it is so much cheaper to carry out the reduction at 1050 to 1150 K that magnesium and sodium are used in preference to hydrogen. At these temperatures, problems associated with reaction between the titanium and the reaction vessel can be solved. The much higher temperature required for hydrogen reduction would give rise to severe problems.

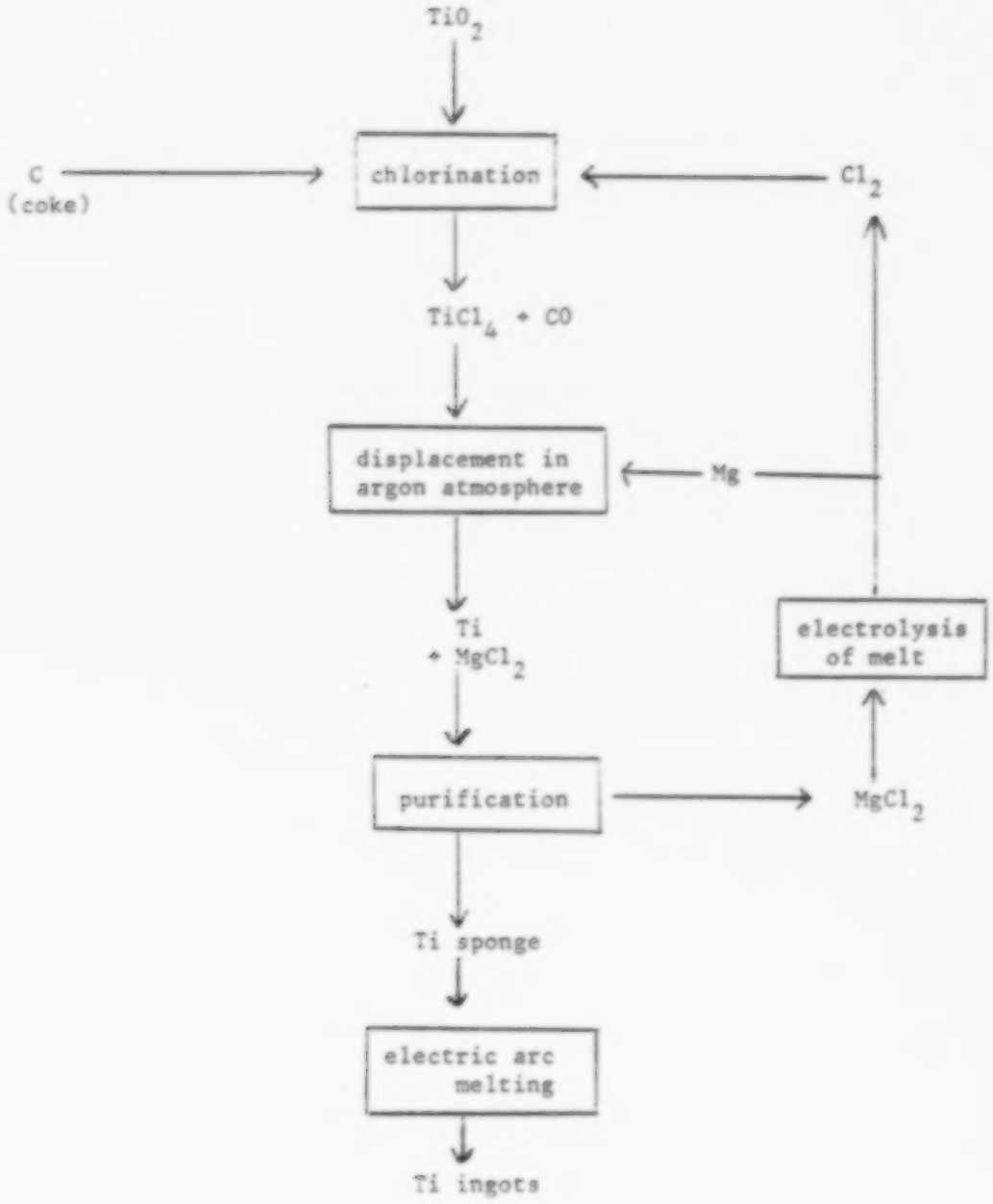
Sodium and magnesium are both used in two different processes pioneered by Hunter and Kroll respectively. The flow chart outlines the processes : your teacher will give you further details.

Both methods are expensive because of the need to chlorinate the oxide before reduction to the metal, and to regenerate the chlorine from the sodium or magnesium chlorides.

* Footnote:

It thus resembles aluminium, which you met in fifth year. Aluminium is obtained by electrolysis, but of the molten oxide. Aluminium chloride cannot be used, because it like $TiCl_4$ is covalent, and consists of Al_2Cl_6 molecules. It sublimes at 451 K, 178°C.

Production of Titanium from TiO_2

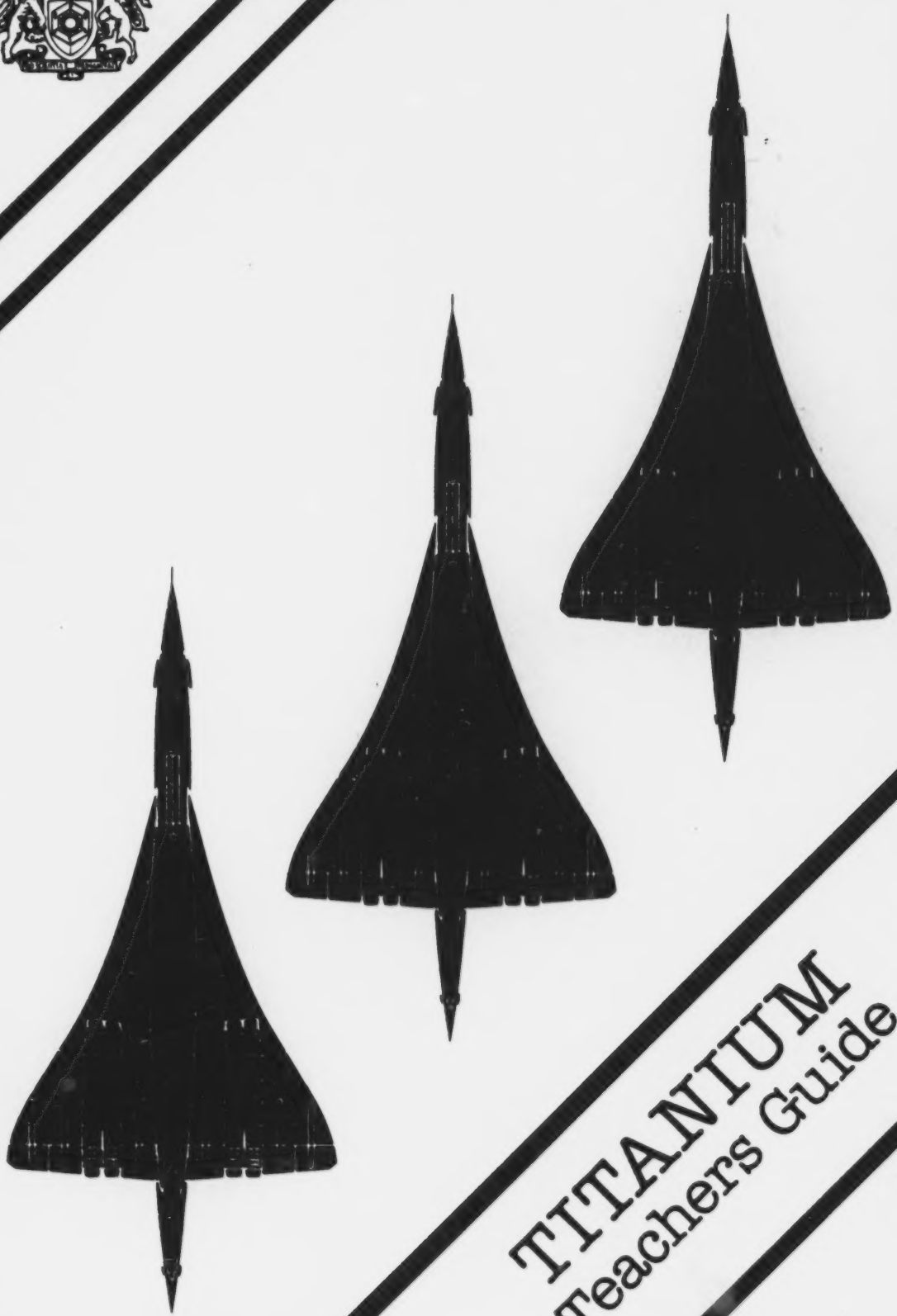


Stages are

1. Concentration of rutile
2. Chlorination of rutile in the presence of carbon to form $TiCl_4$
3. Purification by distillation of the $TiCl_4$
4. Reduction of $TiCl_4$ to titanium using magnesium, or sodium
5. Purification of the crude titanium
6. Electric arc melting to consolidate the crude titanium.

APPENDIX : Thermodynamic Data (at 298 K)

	ΔH_f° ($kJmol^{-1}$)	S° ($JK^{-1}mol^{-1}$)	MP (K)	BP (K)
$C_{(graphite}$	0	5.7	4000	5100
$Cl_{2(g)}$	0	223	172	239
$H_{2(g)}$	0	131.0	14	21
$O_{2(g)}$	0	205	54	90
$Mg_{(s)}$	0	32.5	923	1380
$Mg_{(g)}$	149	148.6	-	-
$Na_{(s)}$	0	51.0	371	1163
$Na_{(g)}$	108	154.0	-	-
$Ti_{(s)}$	0	30.3	1950	3530
$CO_{(g)}$	-111	198.0	68	82
$CO_{2(g)}$	-394	214.0	217	195
$H_2O_{(g)}$	-242	189.0	273	373
$MgO_{(s)}$	-602	27.0	3173	3873
$Na_2O_{(s)}$	-416	72.8	1193	
$TiO_{2(s)}$	-912	50.2	2098	
$TiCl_{4(l)}$	-750	253.0	250	409



TITANIUM
Teachers Guide

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(2) The Chlorination of Rutile

Titanium (IV) oxide is thermally stable and very resistant to chemical attack. It cannot be reduced to the metal using carbon, carbon monoxide or hydrogen. Reduction with electropositive metals (such as sodium, aluminium, magnesium or calcium) is incomplete. .Electrolysis of fused TiO_2 (mp 1825°C) is unrealistic and in any case the melt would contain an unacceptable amount of oxygen. The TiO_2 has to be converted into another, oxygen free, compound which can be reduced to the metal. The intermediate used is titanium (IV) chloride. However rutile cannot be readily chlorinated because the equilibrium position of the reaction (eqn.1) lies far to the left.

$$TiO_2 + 2Cl_2 \rightleftharpoons TiCl_4 + O_2 \qquad (1)$$

In practice, rutile concentrate is chlorinated in the presence of coke at 800-1000°C. The reaction proceeds in either batch or shaft furnaces in a stationary layer - briquetted material must be used. Alternatively it can occur in a fluidised bed using finely ground materials. This latter method results in a continuous operation.

The main products of the chlorination reactions are titanium (IV) chloride and carbon monoxide together with smaller quantities of carbon dioxide and carbonyl chloride.

$$TiO_2 + 2Cl_2 + 2C \longrightarrow TiCl_4 + 2CO \text{ - the main reaction} \qquad (2)$$

$$TiO_2 + 2Cl_2 + C \longrightarrow TiCl_4 + CO_2 \text{ - the most exothermic reaction} \qquad (3)$$

$$TiO_2 + 4Cl_2 + 2C \longrightarrow TiCl_4 + 2COCl_2 \qquad (4)$$

The CO_2/CO ratio depends on conditions. Ideally it should be high to ensure economic use of carbon and energy.

(3) Purification of Titanium (IV) Chloride

The solid impurities ($CaCl_2$, $MgCl_2$, and NaCl) are removed by filtration and remain in the fluidised bed as contaminants.

99.98% pure TiCl is produced by separating the more volatile impurities - chlorides of Cr, Fe, Si, and V - by fractional distillation in argon or nitrogen. Any vanadium present as $VOCl_3$ is removed prior to distillation.

The $TiCl_4$ (fp. -23°C, bp. 136°C) is stored in steel tanks under dry argon. Water must be excluded otherwise rapid hydrolysis takes place - a reaction utilised in smoke grenades:

$$TiCl_4 + 2H_2O \longrightarrow TiO_2 + 4HCl \qquad (5)$$

(4) Magnesium Reduction of Titanium (IV) Chloride

As $TiCl_4$ is a non-conductor it cannot be electrolytically reduced. A chemical reduction technique is used. The initial problems associated with this were largely resolved by Kroll in 1937 who reacted titanium (IV) chloride with magnesium.

In the modern process a thick-walled steel pot (typical dimensions 2.5m high and 2.0m in diameter) is charged with magnesium ingots which have been carefully cleaned by being pickled with hydrochloric acid, washed with water and dried at a low temperature.

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PART 3: NOTES FOR TEACHER PRESENTATION

Note: Pupils should have the diagrams at the end of these sheets to hand during your presentation. Alternatively, you may choose to make ohp transparencies from them.

The greater part of commercial titanium metal is produced by the Kroll Process (magnesium reduction), although in Great Britain sodium is used in place of magnesium to a limited extent. By far the greatest producers of titanium sponge are USSR, USA and Japan, although markets in Germany, Italy, France and Canada are rapidly developing. USSR production is about five times greater than in the USA : until recently, substantial amounts of this were exported e.g. meeting 40% of Europe's requirements. Concern has been felt in the USA at the USSR using all its recent production e.g. for new submarines with hulls four times thicker than their steel predecessors.

Magnesium Reduction

The Kroll Process was developed in the late 1930's. The first commercial plant for general sale opened in 1948 in the USA.

It is a batch process, with the reactor being cleaned after each batch. Cleaned magnesium ingots are stacked in a thick-walled steel reactor, which is then sealed by welding. A water-cooled inlet is left.

The reactor is placed in a furnace, and the air and associated moisture is removed and replaced by argon or helium. The reactor is heated to about 700°C to melt the magnesium, and the $TiCl_4$ is added. The reaction is exothermic, and the addition has to be regulated to maintain the temperature between 800°C and 900°C.

The operating temperature has to be above the melting point of $MgCl_2$ (712°C) but below 1025°C, as above this temperature titanium and steel form a eutectic mixture. In any case, the temperature is kept below 1000°C, as the reactor then suffers little corrosion, due to the formation of a protective iron/titanium layer.

After the addition of some 60% of the stoichiometric amount of $TiCl_4$, the reactor is tapped to remove most of the $MgCl_2$, which lies under the molten magnesium.

Further $TiCl_4$ (to 85% stoichiometric) is added. Still more chloride would increase side reactions such as

$$Ti + TiCl_4 \longrightarrow TiCl_3 \text{ and/or } TiCl_2$$

Titanium is formed as a sponge, sticking to the walls of the reactor above the level of the molten magnesium. Eventually, this bridges the surface, and its weight causes it to fracture and fall to the bottom of the reactor.

The reactor is then cooled and opened. The titanium sponge is removed and crushed: its main impurities are magnesium and $MgCl_2$.

Sodium Reduction

This method is only used in the U.K., and became commercial in 1953, when ICI opened a 50 tons/year plant.

The method is similar to the Kroll Process, except that the sodium is charged into the furnace as a liquid, and a stoichiometric amount of $TiCl_4$ is added. The atmosphere is again argon, with a temperature of 700°C rising to 950°C at the end of the reaction.

Sodium Reduction contd.

Most of the reaction is thought to occur in the vapour phase, and the titanium formed is of higher purity than from the Kroll Process.

Purification of the Titanium

There are two methods in use:

a Leaching i.e. removal of any unreacted magnesium and $MgCl_2$, or of NaCl, with dilute acid. This is used for the sodium reduction method, and can be carried out with a 2% acid solution. Leaching of the sponge from magnesium reduction requires much more acid because of the excess of magnesium used. In fact, 10% acid is used - and this requires an inhibitor to reduce reaction with the titanium. As a result the more costly method of vacuum distillation is normally used.

b Vacuum distillation. Apart from its high cost, its main disadvantage is that the metal sinters and has to be crushed before further processing.

The raw titanium produced is melted by striking an arc between a titanium cathode and the base of the furnace which is made of copper. A vacuum or an atmosphere of helium or argon is used. Current is 250-500 amps per cm of electrode using 40/60 volts.

The high melting point of titanium (1668°C) means that the furnace has to be cooled - either with water or more recently, using a sodium/potassium alloy. The advantage of the latter is that it does not react with the molten titanium should the furnace rupture.

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Data Sources

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PART 4 : TEACHER'S GUIDE

ANSWERS FOR TABLE 1

Reaction	Feasible T (K)	Is it feasible above or below this T?
$TiO_2 + C \longrightarrow Ti + CO_2$	2749	above
$TiO_2 + 2C \longrightarrow Ti + 2CO$	1892	above
$TiO_2 + 2CO \longrightarrow Ti + 2CO_2$	28,595	above
$TiO_2 + 2H_2 \longrightarrow Ti + 2H_2O$	4454	above
$TiO_2 + 2Mg_{(s)} \rightarrow Ti + 2MgO$	9450	below, but Mg not solid at this T
$TiO_2 + 2Mg_{(g)} \rightarrow Ti + 2MgO$	2242	below

Note: Other things being equal, the reaction which takes place at the lowest temperature would be the most economic.

Sample Calculations on Feasibility

a. $TiO_{2(s)} + C_{(s)} \longrightarrow Ti_{(s)} + CO_{2(g)}$

ΔH_f^o	-912	0	0	-394	change = 518 $kJmol^{-1}$
S^o	50.2	5.7	30.3	214	change = 188.4 $JK^{-1}mol^{-1}$

$$T = \frac{518 \times 10^3}{188.4} = 2749K (\text{or } 2476^oC)$$

Feasible above this temperature.

b. $TiO_{2(s)} + 2\ Mg_{(g)} \longrightarrow Ti_{(s)} + 2\ MgO_{(s)}$

ΔH_f^o	-912	2x149 = 298	0	2x-602 = -1204	change = -590 $kJmol^{-1}$
S^o	50.2	2x148.6 = 297.2	30.3	2x27 = 54	change = -263.1 $JK^{-1}mol^{-1}$

$$T = \frac{-590 \times 10^3}{-263.1} = 2242\ K\ (\text{or } 1969^oC)$$

Both negative, so feasible below this T, down to BP of Mg, 1390K.
Because Ti has M.P. 1933K, this prediction is valid from 1390K to 1933K.

Notes:

1. In both examples, the side containing gas is favoured at high temperature. This is because the entropy term $T\Delta S$ favours gases, and increases with increasing temperature.

2. For magnesium, further calculations would be required to ascertain the position outwith this temperature range. These would require to take into account any of the reactants and/or products existing in a different physical state.

   Similar problems arise with sodium : data are given if you wish to try it out.

ANSWERS FOR TABLE 2

Here is the completed table. The figures are approximate, to the nearest 10 kJ or so.

Reactions	ΔG°_{500}	ΔG°_{1000}	ΔG°_{1500}	ΔG°_{2000}
$2\ C+O_2 \longrightarrow 2CO$	-290	-380	-470	-560
$TiO_2 \longrightarrow Ti+O_2$	+810	+710	+610	+520
Adding these gives:				
$TiO_2+2C \longrightarrow Ti+2CO$	+520	+330	+140	-40
feasibility	No	No	No	Yes

ANSWERS FOR TABLE 3

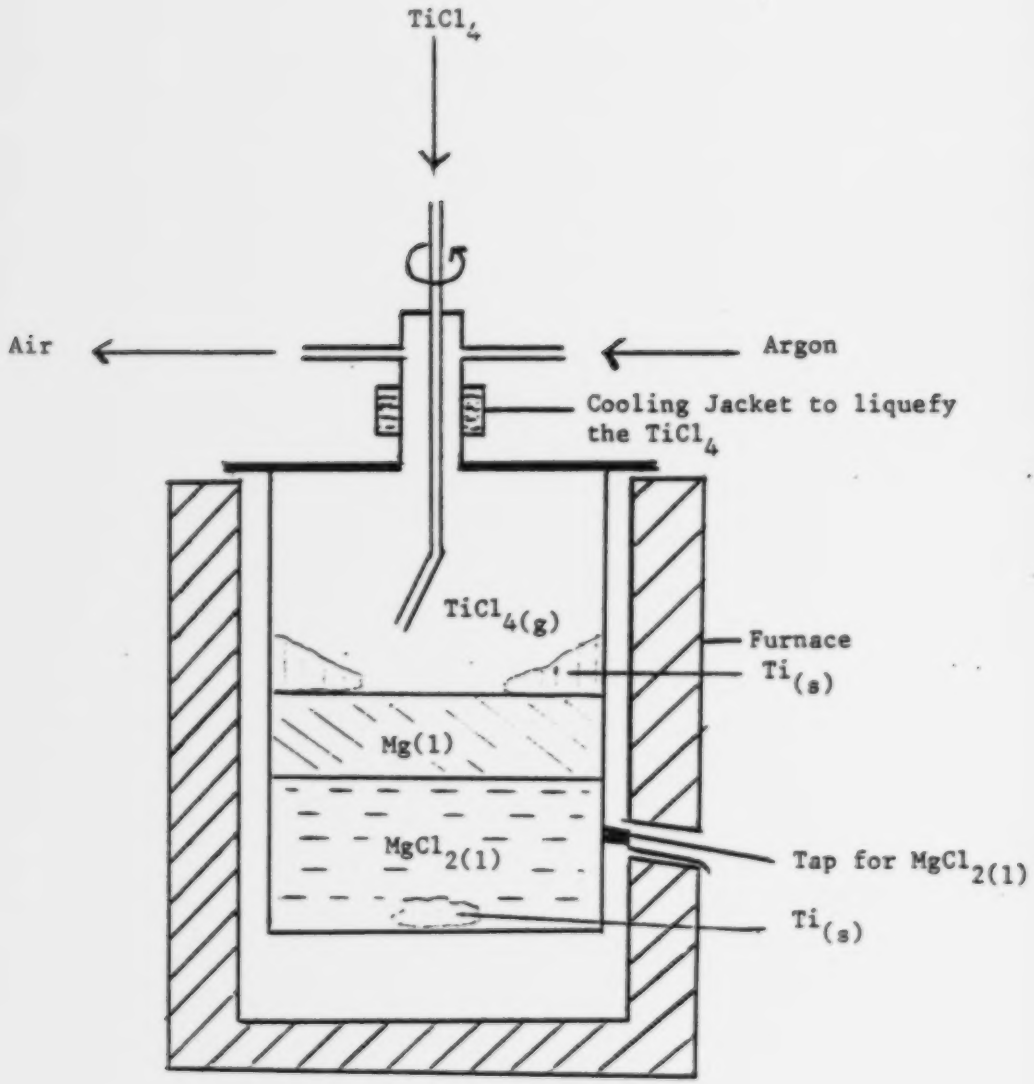
Here is the completed table, to which has been added temperatures obtained by calculation:

Reaction	Feasibility from diagram	Feasibility by calculation
$2C+O_2 \longrightarrow 2CO$	feasible above 1870 K	above 1892 K
$2Mg+O_2 \longrightarrow 2MgO$	feasible below 1900 K	* +
$C+O_2 \longrightarrow CO_2$	feasible above about 2650 K	above 2749 K
$2CO+O_2 \longrightarrow 2CO_2$	feasible at very high T	above 28,600 K
$4Na+O_2 \longrightarrow 2Na_2O$	not feasible	not feasible *
$2H_2+O_2 \longrightarrow 2H_2O$	feasible at high T	above 4454 K

* complicated by changes of state of the Mg and Na

\+ see earlier calculation

Reactor for Magnesium Reduction



$$2\ Mg + TiCl_4 \longrightarrow 2\ MgCl_2 + Ti$$

Typical size: 2.5m high x 2.0m diameter

Data for Magnesium Reduction

Substance	$TiCl_4$	Mg	Ti	$MgCl_2$
Melting Point (^oC)	-25	650	1665	714
Boiling Poing (^oC)	136	1105	3260	1418
Density ($g\ cm^{-3}$) at 850^oC	Gas	1.53	4.3	1.65

At 850^oC the reaction proceeds:-

$$TiCl_{4(g)} + 2Mg_{(1)} \longrightarrow 2MgCl_{2(1)} + Ti_{(s)}$$

Data for Sodium Reduction

Substance	$TiCl_4$	Na	Ti	NaCl
Melting Point (^oC)	-25	98	1665	801
Boiling Point (^oC)	136	883	3260	1465
Density ($g\ cm^{-3}$) at 850^oC	Gas	0.75	4.3	1.52

At 850^oC the reaction proceeds:-

$$TiCl_{4(g)} + 4Na_{(1)} \longrightarrow Ti_{(s)} + 4NaCl_{(1)}$$

although a substantial amount of sodium will be present as $Na_{(g)}$

TABLE .. ADVANTAGES AND LIMITATIONS OF TITANIUM COMPARED WITH OTHER MATERIALS

ADVANTAGES	LIMITATIONS
Light weight and high strength to weight ratio (density ½ steel with strengths fom mild to alloy steels).	High cost of raw and semifinished products due to (a) difficulty of separating metal from ore; (b) necessity to melt under vacuum; (c) care needed during hot working to avoid embrittlement. Difficult to machine – comparable with austenitic stainless steel. Swarf fires can occur with negligent workshop practice.
Exceptional corrosion resistance to oxidising media (e.g. boiling conc nitric acid), moist chlorine gas, aqueous chloride solutions (sea water – no pitting), alkalis (most concentrations and temperatures up to boiling point) and inhibited reducing media.	Attacked by uninhibited reducing media (conc sulphuric, hydrochloric, hydrofluoric, formic and oxalic acids. Aluminium chloride and boiling conc. KOH and NaOH.
Oxidation resistant with retention of useful strength and creep resistance up to 550°C.	
Good cavitation resistance.	Can have pyrophoric reactions with fuming nitric acid containing less than 2% water or more than 6% nitrogen dioxide; liquid oxygen on impact, Anhydrous liquid or gaseous chlorine. liquid bromine, hot gaseous fluorine and oxygen enriched atmospheres.
Special grades have excellent low temperature properties.	Stress corrosion can occur in some alloys if chlorine salts present on stressed parts at high temperatures.
	Strong affinity for hydrogen (above 130°C), nitrogen (above 800°C) and oxygen above 700°C which cause embrittlement.
High fatigue and corrosion fatigue resistance (50% U.T.S.)	Except when fretting occurs.
Most commercial alloys are weldable with varying degrees of weld ductility (some equal to parent metal) – inert gas shielding is necessary for fusion welding and special care must be exercised to avoid contamination.	

OTHER CHARACTERISTICS

Low modulus of elasticity (10.5 – 12.5) x 10^4 MN/m^2 cf 20.9 x 10^4MN/m^2 for steels and for aluminium alloys 6 – 7 x 10^4 MN/m^2.

Low thermal conductivity – less than 5% of copper.
& Electrical conductivity – about 3% of copper.

Low thermal expansion :– 8 – 10 x 10^{-6}/°C between 0 – 500°C.
i.e. half value for austenitic stainless, two-thirds that of low alloy steel and less than half that for aluminium.

Non-Magnetic

THE STORY OF TITANIUM

Written by: D.J. Jones, B.Sc., FRNS
(Handsworth Grammar School, Birmingham)

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THE STORY OF TITANIUM

by

D. J. Jones, B.Sc., FRNS
(Handsworth Grammar School, Birmingham)

Introduction

Titanium occupies 0.63% of the Earth's crust and is the ninth most abundant element (after oxygen, silicon, aluminium, iron, calcium, magnesium, sodium and potassium). It is the fourth most widely used structural metal (after iron, aluminium and magnesium). Distributed throughout the world, economically viable ores exist in Australia, Canada, Finland, Gambia, India, Japan, Malaysia, Norway, Portugal, Senegal, Sierra Leone, Spain, South Africa, USA and USSR. The main ores are rutile (TiO_2), ilmenite ($FeTiO_3$), ilmenite-haematite (found in Canada) and ilmenite-magnetite (found in USSR). Sometimes rutile is found with ilmenite. Titanium ores of little importance at the present time include sphene (a titanosilicate-$CaTiSiO_5$), pyrophorite, perovskite and leucoxene.

1790- A Cornish Clergyman and amateur mineralogist, the Rev. William Gregor, discovered a black magnetic sand which he called 'menacchanite' after his local Parish - Manaccan. This is now called 'ilmenite'.

1795- An Austrian Chemist, Martin Klaproth, concluded that the Hungarian mineral rutile was the oxide of a new element. He called this titanium, after the Titans - the Greek mythological figures symbolising power and strength.

1797- Klaproth also confirmed the presence of titanium in ilmenite.

1826- Although Berzelius produced a sample of impure titanium at this time, over one hundred years passed before pure titanium could be manufactured on an industrial scale.

Reactivity of Titanium

The major problem involved the high reactivity of titanium. It readily forms interstitial compounds with oxygen, nitrogen, hydrogen, carbon, silicon, and iron. Although these elements strengthen the titanium, there is an unacceptable degree of embrittlement accompanied by loss of ductility and resistance to corrosion. The absorption of oxygen and nitrogen is irreversible, whereas that of hydrogen is not. So, in any extraction process the presence of these elements must be carefully monitored and controlled.

First Attempts

1887- 95% pure titanium was prepared by reducing titanium (IV) chloride using sodium. ($TiCl_4$ had been made by Dumas in 1826 by the chlorination of titanium (IV) oxide).

1910- M. A. Hunter at General Electric had obtained 99.5% pure titanium. Here the process involved the sodium reduction of $TiCl_4$, but the product was again hard and brittle.

1913- The Titanium Alloy Manufacturing Co. (USA) became the first commercial producer of titanium. Batches of about 2.25 kg were made.

1925- The first pure sample of titanium was obtained when A.E. van Arkel and J. H. de Boer reacted titanium with iodine at 100-200°C in an evacuated glass vessel and then decomposed the resulting titanium (IV) iodine on a tungsten wire filiament at 1300-1500°C. The product was found to be both soft and ductile, it had a high melting point (1668±10°C) and a relatively low density compared with mild steel (4.51 and 7.86 g cm^{-3} respectively). High tensile strength could be achieved through alloying. Investigations into the chemical and physical properties of the pure metal suggested its potential as a constructional material. However, the van Arkel-de Boer titanium was too expensive to produce on anything other than a limited scale.

The problems associated with an economical large scale manufacturing process for pure, ductile titanium were resolved through the efforts of the Luxembourg born metallurgist, Wilhelm J. Kroll, working in the United States during the 1930's.

1940- His work was published. The United States Bureau of Mines became interested and
1944- this led to the building of a 45kg per week Plant and Boulder City.

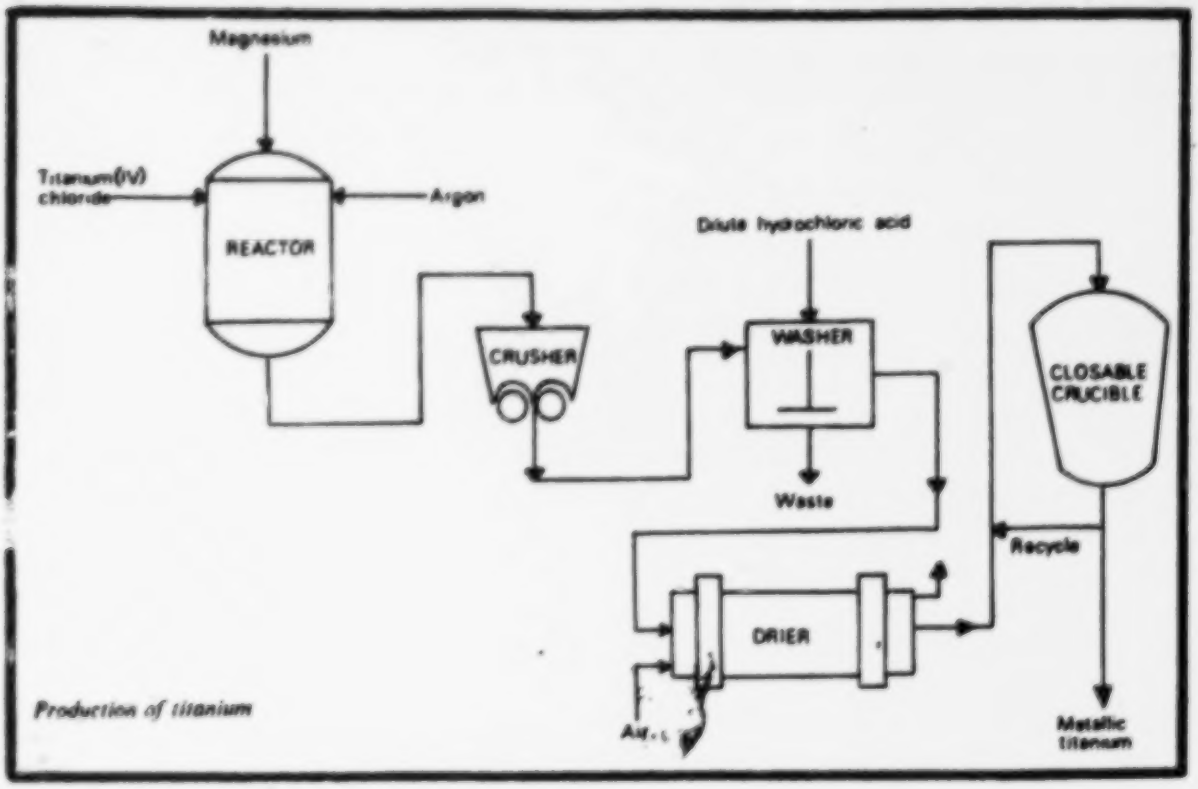
1948- du Pont became the first manufacturer of pure titanium for general sale.

Process Outline

Essentially the developed process involved the following stages:

(1) Concentration of rutile;
(2) Chlorination of rutile in the presence of carbon to form titanium (IV) chloride;
(3) Purification of titanium (IV) chloride;
(4) The reduction of titanium (IV) chloride using either magnesium or sodium;
(5) Consolidation of the crude titanium by arc-melting techniques.

The reasons for this procedure became apparent when the individual stages are studied.



(i) Obtaining and Concentrating the Ore

There are two main ores of titanium which can be used

(a) Rutile - This is the most thermally stable of the three naturally occurring crystalline forms of TiO_2. It occurs in black beach sands produced by the weathering of rocks, mainly in Eastern Australia and to some extent in Florida. Mining is not needed as the material can be obtained by dredging. The sands are concentrated to yield a concentrate containing about 90-98% TiO_2.

(b) Ilmenite - This is essentially an iron titanate, $FeTiO_3$($FeO.TiO_2$), and named after the deposits found in the Ilmen Mountains (USSR). The ore is obtained by open-cast mining from rock deposits. It is crushed, ground and upgraded to between 40-47% TiO_2 using floatation techniques and electrostatic and magnetic separators.

The rutile concentrate is preferred for titanium metal production because it is easier to chlorinate as it is richer in TiO_2 - there are fewer impurities to contaminate the product.

The ilmenite concentrate is used to produce pigment-grade TiO_2 - the presence of impurities is not quite so important.

However, ilmenite is much more abundant and less expensive than rutile. A process was needed whereby the iron content of the ilmenite could be lowered, leaving a product which could be satisfactorily chlorinated. The reason for this was that the United States has large reserves of ilmenite but only limited deposits of rutile.

The reactor is sealed, evacuated, and a protective atmosphere of argon (some plants use helium) introduced before it is heated to about 700°C. Purified liquid $TiCl_4$ is added. Since the reaction is very exothermic the addition must be carefully regulated to maintain the temperature between 850-900°C.

$$TiCl_4 + 2Mg \longrightarrow Ti + 2MgCl_2$$

The operating temperature must be above the melting pot of magnesium chloride (712°C) but below the titanium-iron eutectic m.p. (1025°C). Below 1000°C the pot suffers little internal corrosion due to the formation of a protective, ferrotitanium layer but above this temperature the iron dissolves, damaging the pot and contaminating the titanium.

At first, molten magnesium floats on a layer of magnesium chloride as spongy titanium accumulates at the base of the reactor. As the reaction proceeds the levels of titanium and magnesium chloride rise. The latter is tapped periodically from a valve high on the side of the pot, either by pump extraction or by high argon pressure, ensuring that no air enters the apparatus. This utilises more fully the working volume of the reactor and exposes some of the magnesium entrained in the sponge.

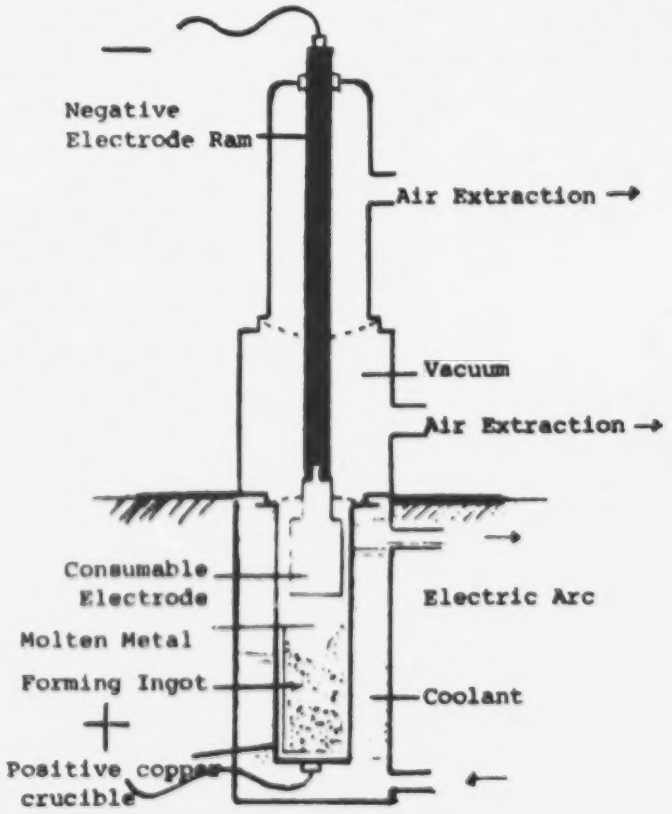


Diagram of a high vacuum, electric arc melting furnace.

Reproduced by permission of the Council of The Institution of Mechanical Engineers from Proceedings of The Institution of Mechanical Engineers Volume 191, 9/77.

Magnesium and chlorine are recovered from the discharged magnesium chloride by electrolysis.

If stoichiometric amounts of $TiCl_4$ and Mg are reacted the yield of titanium is lowered due to the following reactions:

$$3TiCl_4 + Ti \longrightarrow 4TiCl_3 \qquad (7)$$

and

$$2TiCl_3 + Ti \longrightarrow 3TiCl_2 \qquad (8)$$

In practice, a 15-25% excess of magnesium is used.

When the calculated amount of $TiCl_4$ has been added, the temperature is raised to between 900-920°C to complete the reduction of $TiCl_4$ and any subchlorides.

The reactor is then cooled and opened. The 'raw' titanium is removed and crushed. The main impurities at this stage are magnesium and magnesium chloride.

The preferred method of purification is high temperature vacuum distillation at temperatures up to 925°C - a process originally developed in 1939 by Kroll for zirconium. Its disadvantage is that the metal sinters and must be crushed before subsequent processing.

The other method of purification is leaching with dilute hydrochloric acid, probably containing inhibitors to reduce titanium loss, followed by drying. This yields what is known as a 'dirty sponge', due to residual impurities. Hydrogen, liberated by the acid-metal reactions is absorbed reversibly by the sponge. It is removed in the consolidation stage.

(5) Consolidation of the 'Raw' Titanium

The first attempts to convert the 'raw' titanium into usable metal were unsuccussful. The sponge was compacted and sintered, but the product contained residual salts and was not homogeneous. The high melting point of titanium (1668°C) itself posed problems, as did its high reactivity. Induction melting too was unsatisfactory because molten titanium reacts with all known refractories from which traditional crucibles were made. The difficulties were overcome in 1938 by Kroll who adapted the arc melting technique originally devised by Werner von Bolton in 1905 for melting tantalum.

Initially, tungsten arc melting in argon was used, but now double consumable vacuum arc melting is used.

In this process the hearth consists of an enclosed copper crucible cooled either by water, or, better still, by sodium-potassium alloy. One or more blocks of crude titanium sponge are compacted and welded to form the consumable electrode (cathode).

Generally, the furnace is evacuated, but some plants use an inert atmosphere of argon or helium. Melting occurs as a result of a direct arc struck between the electrode and the base of the furnace. As the melting proceeds the current is rapidly increased to between 250 and 500 A cm^{-1} of electrode, at about 40-60 V.

The melt is stirred by rotating the crucible about the axis of the electrode, with the use of a solenoid coil, and this also controls the arc.

Care must be taken to avoid intense arcing on the crucible as this will cause the wall to fracture. The wall separates the melt at 1700°C from the coolant, originally water. This rupture would result (i) in a steam explosion (ii) the molten titanium would react with water to give hydrogen which would explode in contact with air. Hence water-cooled furnaces are operated from behind safety barricades.

In modern plants the coolant is a sodium-potassium alloy and there is no need for blast proofing as molten titanium does not react with the coolant. A failure of the coolant supply would also cause the wall to rupture.

The ingots produced are usually remelted in a larger crucible where they function as consumable electrodes. This improves homogeneity and further reduces the magnesium, magnesium chloride and hydrogen content of the titanium.

The use of a consumable electrode (first developed for molybdenum in 1947) gives a higher melting rate, produces more homogeneous ingots and enables plant equipment to be simplified.

Vacuum melting enables volatile impurities (e.g. hydrogen) to be removed more effectively.

ICI and Titanium Manufacture in Britain

Britain's Titanium Industry is based on three companies: ICI, BTP and IMI. ICI became interested in titanium manufacture in 1945. By 1948 ICI General Chemicals Division (now ICI Mond Division) had produced some by the magnesium reduction of titanium (IV) chloride for assessment by ICI Metals Division (now IMI). An experimental plant was built at Widnes in 1951 and the following year the decision was taken to build a 100 tons/year plant. Pidgeon Process Magnesium (produced when calcined dolomite is reduced by ferrosilicon in an electric furnace) was used in this, rather than electrolytic magnesium, since it contained less iron and manganese

However, in 1951 ICI began to develop its own process based on the sodium reduction of $TiCl_4$ and two years later a 50 tons/year plant came on stream.

In 1955 a 1500 tons/year plant was built at Wilton (Billingham) after Government consultations, although it closed 1960-1964 because of Government stockpiling.

Sodium reduction was not developed in the United States because it was thought that the sodium reaction, being more energetic, would be difficult to control.

Today titanium is produced by ICI Mond Division at its Bain Works. Salt from the Weston Plant at Runcorn is electrolysed at the Cassel Works using the Downs Process to produce sodium and chlorine. The chlorine is used by British Titan Products at Billingham to chlorinate rutile, in the presence of coke, to produce $TiCl_4$. The sodium used should be as pure as possible and although the presence of potassium or calcium

is not a problem, it is essential that the material is free from the sodium carbonate, hydroxide, hydride and oxide and calcium nitride and oxide.

$TiCl_4$ is passed into a mild steel reactor pot (batch size about 1.3 tonne Ti) containing molten sodium, in an argon atmosphere, at 650°C. The exothermic reactions cause the temperature to rise quickly to 800 - 900°C as the $TiCl_4$ is reduced to $TiCl_3$ and $TiCl_2$. The reduction of $TiCl_2$ and TiCl is slower, so in the final stages of the process the temperature is raised to about 950°C to complete the reduction.

Although the reduction process takes about 36 hours it is usual to leave the pot in position for about 50 hours. The reactor is removed and left for four days to cool. It takes about a day to remove the sodium chloride-titanium mixture by mechanical means.

The overall reaction is: $TiCl_4 + 4Na \longrightarrow Ti + 4NaCl$ (9)

The mixture is crushed, leached with dilute hydrochloric acid, centrifuged and dried to give titanium powder.

Compared with magnesium reduction, sodium reduction has many advantages. It is possible to react the stoichiometric quantities of $TiCl_4$ and Na (consider leaching a sodium-titanium mixture!); the process is more efficient and produces titanium of higher purity. The product is more resistant to hydrolysis, and an acid pH -- 2 reduces hydrolysis. There is, therefore, no need to use expensive vacuum distillation, involving high capital outlay and high operating costs. Sodium chloride has a higher boiling point (1465°C) than magnesium chloride (1418°C).

Since the product is granular it can be more readily compacted into electrodes for arc melting than Kroll sponge, but it is harder due to a higher oxygen content.

ICI's investigations into arc melting began in 1948 and in 1954 a 150 tons/year pilot melting plant was in operation. The next year a 1500 tons/year production plant was built in Birmingham. In 1957 double consumable vacuum arc melting was introduced. Blast proofing appeared following an explosion in 1956, while an explosion on a 2 ton furnace in 1966 (no injuries) led to the replacement of water as a coolant, by a sodium-potassium alloy.

ICI supply titanium powder in 67 kg deums and 2.2kg packs. The powder is dangerous because it can be ignited by sparks, friction or heating. It burns readily in air, nitrogen, carbon dioxide, halogen vapours and in many organic chemical vapours. Titanium fires are most effectively extinguished by smothering with dry sodium chloride.

Most of the titanium is used by IMI (Titanium) at Witton (in Birmingham). There it is converted into ingot and wrought forms. Rolls-Royce (1971) Limited and other manufacturers use titanium alloys for aeroengines and defence applications. Since the Bain Works is registered with the Ministry of Defence, quality control is strict.

Uses of Titanium

The metal resembles iron and nickel in being hard and refractory. It exists in two allotropic modifications, α-Ti below 882.5°C which has a hexagonal close packed structure, and β-Ti above which is a body centred cuboid.

It is an excellent structural material due to its high melting point and relatively
(1) low density. It is particularly useful for aerospace product-engines, airframes etc.

Its properties may be improved through alloying. As early as 1826 Mushet had patented the use of titanium in steels, although this use did not seriously begin until 1900.

In 1935 welding rods with titanium coatings containing titanium (IV) oxide were introduced.

IMI initiated Britain's research programme into titanium alloys during 1953.

The most popular alloy used to date has been Ti-6Al-4V which has given an all-round improvement in properties.

Ti-5Al-2.5Sn was used for the Mercury and Gemini space capsule structural frames. This latter alloy together with Ti-8Al-IMo-IV have been used at moderately elevated temperatures.

(2) Although the metal is very electropositive it is rendered passive due to the presence of a thin, coherent, protective oxide coating. Oxidising environments do not impair the layer, and neither do aqueous solutions containing Cl^-, OCl^-, S^{2-}, SO_4^{2-}, NO_3^- and PO_4^{3-} ions. As with aluminium, if the film is broken then corrosion of the metal occurs. This happens in reducing conditions or in the presence of hot concentrated $AlCl_3$, $CaCl_2$ or $ZnCl_2$ which hydrolyse to yield non-oxidising acids. It is possible to inhibit corrosion by suitable alloying, the Ti-0.2Pd alloy being particularly corrosion resistant.

The metal has found wide use in chemical plant, the oil industry, power stations and desalination equipment. It has also been used in electrochemical equipment. In the Chlor-alkali Industry the graphite anodes used in Mercury and Diaphragm Cells have been replaced by platinum coated titanium electrodes. This has solved a number of problems, making the process more economical and saving on power consumption. The precious metal coating is important because without it the titanium does not make an effective anode.

It is also used in the electrolytic purification of copper where it functions as a cathode blank upon which the copper is deposited.

Titanium (10)

The metal appears to be chemically inert in all natural environments, including body fluids and since 1954 titanium has been used in the manufacture of

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prostheses eg hip prostheses, replacement joints etc.

The Role of the USSR in Titanium Production

The key country in titanium sponge production is the USSR with an estimated production level of about 40,000 tonnes per annum. This represents more than twice the production of the rest of the world combined. In 1974 USSR supplied 40% of the European sponge requirements, and the USSR exports accounted for 20% of the non-communist world's consumption. The USSR production was 400% more than

(3) more than the United States titanium production, and 1600% more than Britain.

Titanium for the Future

- Existing plant

ICI Mond Division is phasing out production of titanium. The reasons for this are:

(a) the existing plant is 25 years old and would need heavy capital investment to bring up-to-date.

(b) the plant is the second smallest in the world

(c) the titanium market will continue to suffer from the cyclical demand pattern of the aerospace industry.

(d) the titanium business - for ICI - has been consistently unprofitable. There is no incentive to continue titanium manufacture.

However, ICI has agreed to operate existing plant until 1982 - provided Rolls-Royce underwrites the deficit. Rolls-Royce requires sodium-reduced titanium granules, rather than Kroll Sponge, for the RB 211-535 engine developed for the Boeing 757.

- Government involvement

A new titanium granule processing plant is to be built in Hartlepool by the National Enterprise Board, in conjunction with Rolls-Royce and Imperial Metal Industries. The plant will cost about £30 million (around £20 million is to be supplied by the NEB), and will produce more than 5,000 tonnes per year of titanium granules. The company will be known as 'Cleveland Titanium Limited' and as such will be one of the NEB's largest investment projects. The NEB is seeking a private enterprise partner to take over its stake in the venture - so far without success. Despite a world shortage of titanium it is proving difficult to convince potential backers that the plant will become competitive on the international market

- Titanium shortage

The Soviet Union has virtually ceased exporting titanium and this has caused concern in the United States. The Soviet Union has begun to use much more titanium to make new military submarines. These are capable of operating

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at greater depths than existing submarines and have walls four times thicker than those made currently from stainless steel.

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Erratum

replace titanium (IV) throughout by titanium(IV)

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TITANIUM AND ITS ALLOYS.

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INTRODUCTION

1. The following presents a short introduction into the manufacture of titanium and its alloys. Recovery of titanium metal from its ores is detailed, as are the manufacture of castings, problems associated with contamination of the materials and the development of fabrication aspects. A brief outline of the uses of titanium in both the aero and Naval disciplines is also given.

2. Amplification of the features discussed is made by inclusion of a selection of references covering all aspects associated with the manufacture and development of the alloys.

Titanium Occurrence

3. Titanium is the fourth most abundant structural metal (0.6% of the Earth's crust) available to us, being exceeded only by aluminium, iron and magnesium. It is almost always associated with oxygen in the natural state.

4. In spite of its wide distribution, titanium is only comparatively rarely found in a sufficiently concentrated form to be of interest to the extraction metallurgist (e.g. in minerals ilmenite, titano magnetite and rutile). Naturally occurring ilmenites consist of haematite particles in a matrix of ilmenite while titano magnetites are magnetite containing lathes of ilmenite ($(Fe\ Ti)\ O_3$). Weathering breaks down the ilmenite structure into finely dispersed particles of titanium and ferric oxides.

5. Titanium dioxide ($Ti\ O_2$) occurs in three allotropic forms; rutile, anatase and brookite, rutile being by far the most common naturally occurring form. All three allotropes are found in magmatic rocks In certain parts of the world rutile, liberated from decomposition of the magmatic rocks is deposited on shores by action of the sea to give significant concentrations. Concentrations of ilmenite, titano magnetite or rutile, which warrant commercial mining are found principally in Norway, Sweden, Finland, the Transvaal, Ilmen mountains of USSR and certain regions of North and South America. Extensive beach concentrations of either rutile or ilmenite are situated in Australia, and Southern India. Lesser deposits occur in Japan, Malaya, Ceylon, Florida, New Zealand and Natal.

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Recovery of Titanium Metal from its Ores

6. Separation of ilmenite and magnetite from the siliceous gangue present in crushed and ground ores is carried out by either froth flotation, specific gravity or magnetic methods. Beach sands containing rutile and ilmenite are usually concentrated by flotation or electrostatic methods; the mixture of rutile and ilmenite so obtained is in turn separated into its two components by a magnetic method, rutile being non magnetic.

7. Typical analysis of ilmenites of both high and low titanium content and a titano magnetite are shown below.

Component	High TiO_2% Ilmenite	Low TiO_2% Ilmenite	Titano Magnetite
TiO_2	57.5 - 61.0	38.5 - 41.5	8.0 - 11.0
FeO	9.0 - 19.0	28.0 - 31.0	30.0 - 34.0
Fe_2O_3	20.0 - 26.0	18.0 - 21.0	46.6 - 50.0
MgO	0.5 - 1.2	3.5 - 4.5	1.5 - 3.0
CaO	0.1 - 0.2	0.3 - 1.0	0.6 - 1.5
$Si O_2$	0.5 - 2.0	2.0 - 9.0	1.5 - 4.5
Al_2O_3	1.0 - 2.0	2.0 - 4.0	3.0 - 6.0
ZrO	0.5 - 2.0	0.0 - 0.05	-
Nb	0.01 - 0.15	0.01	-
V	0.05 - 0.4	0.1 - 0.2	0.6 - 1.0
Cr	0.05 - 0.2	0.1 - 0.3	2.0 - 0.4
Mn	0.05 - 0.4	0.1 - 0.3	0.4

8. Rutile after separation from siliceous material is by far the purest form of titanium oxide, containing 91-99% of the oxide with small amounts of zirconium, niobium, vanadium, chromium, iron, silicon and aluminium.

Reduction of Titanium Dioxide ($Ti O_2$)

9. None of the attempts to reduce titanium dioxide directly to titanium metal have been sufficiently successful for commercial use. The difficulties are that:-

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(a) the compound has an exceptionally high heat of formation (approximately 800KJ/mol)

and, (b) titanium in common with other transition elements of groups of the Periodic Table, is capable of taking a large quantity of oxygen into solid solution.

Both of these facts are of considerable practical importance and prevent the use of any conventional method of reducing the ore to metal since the reducing agent must not only be capable of producing a metal-oxygen solution from a highly stable oxide, but must also be able to overcome the increasing chemical affinity of the O_2 present in the metallic solution as the concentration of dissolved O_2 is reduced.

10. Active reducing agents such as magnesium, calcium and barium all have a high affinity for O_2 and can, in principle, be used to produce low O_2 level titanium. Calcium, for example, can at 1000°C give a product containing only 0.1% O_2. It is for practical reasons not yet used on a wide commercial scale.

11. The great difficulties involved in removal of O_2 from titanium bearing ores led to the development of an extraction process which starts with an O_2 free material. At the present time, by far the greater part of titanium produced commercially relies on the reduction of titanium tetrachloride with magnesium to give titanium.

Titanium Tetrachloride ($TiCl_4$)

12. Titanium tetrachloride is prepared by the combined reduction and chlorination of rutile according to the equation

$$TiO_2 + 2Cl_2 + 2C \rightarrow TiCl_4 + 2CO$$

The rutile is mixed and ground with coke and the mixture bound with coal tar. This mixture is heated in a kiln to remove volatile materials and the resulting hard porous mass is crushed, briquetted, and fed into a chlorinator plant which operates at 800°C. $TiCl_4$ which boils at 136°C is evolved with CO, CO_2 and excess chlorine, at the top of the chlorinator and is collected in a condenser.

13. The major difficulties in the chlorination process arise from the fact that rutile contains small quantities of a large number of other oxides which are also reduced and chlorinated during the production of $TiCl_4$. Non volatile and volite chlorides are formed; the former by coating ore particles and the latter are distilled over and, on condensing, can dissolve.

14. The cost of producing pure titanium tetrachloride from expensive rutile is high and contributes in no small measure to the high price of titanium metal.

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15. Ilmenite is a cheaper source of TiO_2 than rutile, however, a difficulty experienced in processing it to yield $TiCl_4$ lies mainly in the separation and disposal of the high iron content of the ore. Ilmenite cannot be directly chlorinated since not only are large quantities of chlorine absorbed in producing iron chlorides but the volatile ferric chloride evolved would rapidly choke the outlet of the chlorinator and stop the plant.

16. It is also not possible to separate the iron and titanium oxides in Ilmenite by mechanical methods since they are in solid solution with one another and therefore chemical 'separation' is required. Ilmenite is readily soluble in sulphuric acid, but the resulting solution contains considerable quantities of ferric sulphate which must be converted to the ferrous salt before the titanium can be precipitated as the oxyhydrate.

Reduction of Titanium Tetrachloride

17. $TiCl_4$ can be reduced to give titanium sponge by hydrogen, calcium, sodium and magnesium. The stable compound reduction is only possible at high temperatures (2000°C for H_2). The latter 'materials' are exothermic and therefore it is possible to produce 'sponge' at temperatures much below that necessary for hydrogen reduction.

18. Although sodium reduction processes for the production of titanium metal from $TiCl_4$ are in industrial use, by far the greater part of the titanium available at present time is produced by the Kroll magnesium reduction process. The basic reaction is:-

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$$

In the manufacture of titanium sponge $TiCl_4$ and Mg are time fed into a purged and inert gas filled reactor. The vessel is heated slowly to allow gases evolved to be removed prior to the Mg becoming sufficiently hot to react with them. Inert gas pressure is maintained above 1 atmosphere. When the magnesium is molten, $TiCl_4$ is admitted. Reduction then begins, the heat generated by reaction being taken care of in controlling operating temperatures between 800° and 900°C.

19. Titanium metal is deposited preferentially around the walls of the 'reactor' above the level of liquid magnesium. As reaction proceeds a sponge-like mass of titanium grows across the crucible eventually forming a continuous bridge.

20. After production of the sponge the reaction product is cooled in situ. Solidified masses of magnesium chloride, residual magnesium and titanium are removed in a dry atmosphere (so as not to contaminate the finely dispersed Ti sponge) and the titanium sp onge removed by 'chipping out'. Magnesium chloride is recycled to produce Mg and chlorine. The products are again used in the production of sponge and $TiCl_4$.

26. For many of these products titanium castings offer improved material utilisation, lower metal removal costs, and the elimination of welding as compared with forged and/or fabricated parts.

27. The need for heavy financial investment in foundry equipment and development technology has limited the number of foundries producing titanium castings. In the USA there are 6 titanium casting facilities - three using conventional techniques and three investment.

28. Castings are presently avaulable on a large scale in commercially pure, Ti + 0.2% Pd, Ti-6Al 4V, and Ti-5Al-2.5Sn titanium alloys. However, there is no technical reason known at present to preclude the casting of any other commercial or experimental alloy. Details of geometrical limitation of conventional (rammed graphite) and investment titanium castings are as follows:-

Maximum Size Limits of Individual Centrifugal Castings

Weight	159 Kg	350 lb
Height	0.71 m	28 in
Length	1.27 m	50 in
Width	0.66 m	26 in

Maximum Size Limits of Centrifugal Centre-Axis

Weight	272 Kg	600 lb
Height	0.76 m	30 in
Length	1.65 m	(65 in) diameter
Width	1.65 m	(" ") "

Titanium Properties and Applications

29. The outstanding properties which make titanium such an attractive material are its very high strength/weight ratio and its exceptional resistance to corrosion.

30. Unalloyed titanium has about 56% the density of steel and a tensile strength of 300-750 N/mm^2 (20-48 $tonf/in^2$), which can be raised to over 1250 N/mm^2 (80 $tonf/in^2$) by alloying. The elastic modulus of titanium is roughly half that of steel, but nevertheless it is much greater than that of aluminium or magnesium, metals used structurally in the aircraft industry for many years.

31. In general, the strength of titanium decreases with temperature, but it maintains useful properties above the temperature at which other light metals can be used. The effective limit for current titanium alloys is about 500°C, although this range will extend as alloys develop.

32. Titanium can withstand attack by a wide variety of aggressive media and it has extremely high resistance to pitting and stress corrosion cracking (depending on alloy and O_2 content). In most applications

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Electrolytic Methods of Producing Titanium

21. Production of titanium metal by the electrolysis of aqueous solutions of titanium compounds is unlikely to prove successful since all such compounds are readily hydrolysed. Some earlier work did, however, show that the electrolysis of acidified aqueous solutions of titanium sulphate reduced the titanium from the quadrivalent to the trivalent state and that thin deposits of oxy-salts were sometimes formed.

22. Investigations are continuing into processing production of titanium from electrolytic reaction using titanium dioxide and titanium halides. Perhaps the most significant of these is the 'small scale production' method used in the USA in which $TiCl_4$ is used as a starting material and titanium tri- and di-chlorides are produced in the course of reaction. A two stage cell containing one anode and two cathodes is used. $TiCl_4$ is reduced to a lower chloride at one of the cathodes and titanium metal is desposited on the other. The electrolyte consists of strontium chloride and sodium chloride and the bath is heated under an inert gas atmosphere. Gaseous $TiCl_4$ is bubbled through the electrolyte near the reduction cathode where the reaction

$$TiCl_4 \longrightarrow TiCl_2 + Cl_2$$

occurs under the right current flow conditions. Titanium dichloride at the reduction cathode must be dispersed throughout the electrolyte before satisfactory metal deposition occurs.

23. In summary by far the greater part of all commercial titanium metal is produced by the Kroll (magnesium reduction) method although in Great Britain limited production is carried out using the sodium reduction method. By far the greatest producers of titanium sponge are USA, USSR and Japan, although markets in Germany, Italy, France and Canada are rapidly developing. IMI (Kynoch) represent the largest UK supplier (5000 tons/year).

Cast Titanium Alloys

24. From production of titanium sponge the material is collected and if necessary (to produce alloys) alloyed with chemically controlled amounts of additives or scrap to produce higher strength titanium alloy castings.

25. Until recently, problems with vacuum melting, an essential prerequisite in the production of titanium, mould materials and metal mould reaction had prevented the production of titanium castings on an industrial scale. However, recent improvements have made both conventional and investment castings a commercial reality for parts which were formerly welded constructions or forgings, as well as providing forging blanks and new components where the freedom to produce the complex forms allowed by casting permit the cost effective use of titanium. Typical examples are impellers and pump housings and valves for the chemical industry. Corrosion resistance is superior to stainless steels.

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33. The performance of titanium in such corrosive agents as sea water, chlorine, chlorite and hypochlorite solutions, nitric acid, chromic acid, metallic chlorides, sulphides and organic acids is remarkable. Anodically protected by a small impressed voltage, titanium withstands attack by a still wider range of aggressive chemicals. The resistance of the material to dilute reducing acids is improved by the addition of a small quantity of palladium.

34. The physical properties of pure titanium show several interesting differences from those of other commercially employed structural metal. Pure titanium undergoes a crystal transformation at 882°C. Above this temperature it has a body-centred cubic structure known as the beta (β) phase, below it has a close packed hexagonal structure known as the alpha (α) phase. The increased number of slip phases in the α phase means that the material is ductile at room temperature and can be deformed 95% or more between anneals. Melting point for the metal is 1660 ± 10°C.

35. A comparison of titanium properties with other selected and similar metals is given below. The data represents average information used by designers in developing structural requirements for components in the aerospace, aero, petrochemical industries and Royal Navy Surface Ships and Submarines.

Atomic Number 22			Atomic Weight 47.9		
Crystal Structure Below 882°C Close Packed Hexagonal (α)				Above 882°C B.C.C. (β)	
	Titanium	Al	Cu	Fe	Mg
Melting Point °C	$1660^{+}_{-}10$	660	1084	1335	650
Density (g/cm^3)	4.51	2.7	8.94	7.86	1.74
Thermal Conductivity ($Cal/cm/cm^2/°C/Sec$ at 20°C)	.0407	.57	.92	.17	.35
Specific Heat (Cal/g/°C at 50°C)	0.126	0.211	0.093	0.109	0.245
Coefficient of Thermal Expansion	8.9	24	16.4	11.9	25.7
Magnetic Susceptibility (10.6 c.g.s. units/g)	+3.43	+.65	-.086	Ferro Mag-netic	+.55
Normal Electrode Potential (Volts)	-1.75	-1.67	+.52	-.04	-2.38
Elastic Modulus ($10^6 lb/in^2$)	15	10	17.5	29	6.5

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36. Mechanical properties of titanium are affected by small amounts of oxygen and nitrogen in solid solution. It is, therefore, possible to produce a number of grades of commercially pure titanium with mechanical properties suited to the different applications for which the material is intended. A range of ICI titanium alloys is indicated in the table below. Variations in mechanical properties are also identified.

	ICI Titanium 115	ICI 120	ICI 125	ICI 130	ICI 150	ICI 160	
Tensile Strength (tonf/in^2)	26	30	25-35	30-40	35-45	40-50	
0.1% Proof Stress (min ton/in^2)	13	15	18	22	25	30	
Elongation (% on 4$\sqrt{A}$)	30	25	22	20	18	18	
Young's Modulus (10^6lb/in^2)	15-17	15-17	15-17	15-17	15-17	15-18	
Fatigue Limit (% of UTS)	50	50	50	50	50	50	
Bend Radius (180° Bend)	1t	1t	1t	1t	1t	2t	

37. The physical and mechanical properties of titanium are altered by the addition of other metals. As an example, a commonly used alloy ICI Titanium 318A contains 6% aluminium and 4% Vanadium. It has high room temperature strength and its properties can be somewhat modified by heat treatment either to give maximum strength or to obtain optimum creep resistance at 300-400°C.

38. At room temperature Ti (6Al/4V) has a duplex structure consisting of α & β structures. At higher temperatures this progressively transforms to an all-beta structure (complete at 980 $\pm$ 20°C).

39. The β phase is easier to deform than the α phase and there is no great loss in tensile properties on forging in the β phase field. Nevertheless the best combination of strength and ductility is obtained after forging in the range 800-850°C and it is normal for about 50% deformation to be carried out in this range. Typical mechanical properties are shown below for ICI titanium 318A.

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Tensile Strength (Min)	62 tons/in^2
0.1% Proof Stress (Min)	57 ton/in^2
Elongation (Min)	10% on $4\sqrt{A}$
Fatigue Limit	60-65% APP of t.s
Bend Radius (180^o bend)	4t

Effects of Common Impurity Elements

40. The presence of very small quantities of interstitially-soluble umpurity elements in titanium (oxygen, nitrogen and carbon) have a great strengthening effect and ultimately a very marked embrittling effect on the metal at room temperature.

41. Oxygen and nitrogen cause greater hardening in titanium than equivalent atomic concentrations of carbon and the slightly greater hardening produced by nitrogen compared with oxygen is certainly a real effect. Thus, it is essential to control the amount of ingress throughout all aspects of processing. This includes forging (although the embrittled layer is normally removed) and all forms of joining.

42. Hydrogen leads to the formation of a fine dispersion of brittle hydride particles distributed throughout the metal and has thus an adverse effect on the impact properties of the metal.

43. Iron is present in commercial titanium to the extent of about 0.1 - 0.2 wt %. Increasing iron has the effect of raising the UTS at expense of elongation. For example, UTS can increase from 48 x 10^3 lb/in^2 to 60 x 10^3 lb/in^2 as Fe increases from 0 - 0.5%; elongation correspondingly falls from 52% to 38% (% on $\frac{1}{2}$in).

44. The effects of impurities can be seen in increased tendency to stress corrosion cracking in sea water (O_2 > 0.25%), a reduction in impact resistance and fall off in corrosion resistance. It is essential therefore to consider these aspects throughout all aspects of fabrication.

Applications

Aircraft

45. Most aircraft developed for military or civil use since the early 1950's contain components made from titanium or titanium alloys. Titanium is thus a well established material of construction in the aerospace industry. The main reason for increasing use of the metal in this demanding field is its attractive strength/weight ratio at room and elevated temperatures.

46. In gas turbine engines, titanium alloys are used extensively for such components as compressor blades, discs, casings, by-pass ducts, engine cowlings and exhaust shrouds. Air frame uses include structural forgings, fasteners, hot-air ducting, heat shields and hot-area skinning.

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Chemical

47. Resistance to corrosion in a wide range of natural or synthetic environments makes titanium an ideal material for many existing and new chemical units. It is used as a lining or as a primary constructional material for vats, driers and reactor vessels, for tubular or plate-type heat exchangers, for condensers in the power-generation industry, and for pumps, valves and many other chemical components.

48. Titanium's resistance to body fluids is so good that it is being increasingly used for a wide variety of surgical and dental implants.

Electrochemical Processes

49. Titanium is ideal for making anodising jigs since the characteristics of the anodic film enable continued use of the jigs to be made without stripping. If required for use as a non-consumable anode, particularly in the chlorine industry, a thin coating of platimum or other noble metal will allow heavy currents to be carried. Other uses in metal-finishing plant include coils and immersion heaters, anode baskets and jigs.

Engineering

50. A high strength/weight ratio leads to reduction of centrifugal or inertia stresses where titanium is used in rapidly moving parts such as centrifuges, connecting rods, or steam-turbine blades and lacing wire. Chemical and mechanical properties make it attractive for springs, valves and seals, etc. A short half-life makes titanium useful for many nuclear-reactor components and ancillary equipment.

Defence

51. The high strength/weight ratio, good corrosion resistance in sea water and enhanced impingement and erosion resistance of the alloy make titanium suitable for a range of system, components and fittings. As examples, the material and alloys are used for gas turbine uptakes and blades, diesel engine exhaust and muffler systems, sea water system, Hull valves, fasteners, condenser and heat exchanger tubes and tube plates.

52. In the application of titanium to sea water systems it must be realised that the material is susceptible to Marine fouling and therefore under low flow conditions it is necessary to give consideration to electro-chlorination, copper dosing or cathelco (copper/aluminium) systems to poison the various crustaceans. In addition, titanium is a noble material and coupled with most other materials in an electrolyte it behaves as the cathode.

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53. In summary, the tables appended at annex indicate the advantages and limitation of titanium and alloys.

Welding of Titanium

54. CP titanium and most titanium alloys are being welded daily with excellent results. However, just as there are rules for welding other common structural metals, so are there certain rules and procedures to follow for welding titanium.

55. Titanium is susceptible to property change on the introduction of oxygen, hydrogen, carbon and iron. It is, therefore, necessary to understand the influence these elements have on the performance of the material and take necessary precautions during the joining of cast or forged sections of material.

56. Titanium and its alloys can be joined by any of the recognised welding/brazing processes. These include arc, spot, seam, flash, pressure, friction, electron beam, vacuum brazing, torch brazing, etc. Precautions must be taken to ensure that adequate preparation and control during welding is exercised. Control in welding relates to nozzle shrouding, purging prior to and after welding, shielding the weld when at temperature and control of cleaning and finishing procedures.

57. Preparation for welding should require only use of a dilute caustic wash with water rinse or an alcohol or acetone water wash. Chlorinated solvents such as tri-chloretheyne (remains of which may cause cracking in high strength alloys) are not to be used.

58. Prior to welding the areas to be joined are to be covered with an inert gas (argon, helium) to ensure no contamination with oxygen/hydrogen. Where full penetration welds are expected then the back surface should also be shrouded throughout the joining process. (This does not apply to welds carried out in an inert/vacuum chamber, i.e. electron beam welding.

59. Welding is by either Tungsten Inert Gas (TIG) or Metal Inert Gas (MIG) processes normally. The 'guns' are modified at the heads to provide a leading and trailing shield for the welds, the trailing shield being maintained until the temperature falls to 300°C.

60. Use can be made of the weldability of Titanium and its alloys by the introduction of cast/weld techniques where smaller cast sections of a component are made and the sections joined together by a controlled selected process.

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The Way Ahead

61. Titanium offers distinct advantages over many other conventional materials. Its high strength/weight ratio combined with superior corrosion resistance makes its application to marine and chemical environments most desirable and suitable.

62. It has been established that the USSR have developed an 'all-titanium-submarine' although the exact details are not known. To have achieved this would mean the development of technology for forming or fabricating large plates, stiffeners, beams, I and T-section fittings. The advantages are reported as being a submarine which can operate at 40 knots at 3000 ft. Such technology indicates that in the defence area only limited progress has been made and it is in this area where the future of the alloys will rest.

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